REVIEW

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Magnetic superconductors

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Abstract : The interplay between superconductivity and magnetism is outlined The elements and phenomena related to these magnetic superconductors are introduced. The rare earth ternary superconductors, re-entrant superconductors, the weak-itinerant ferromagnetic superconductor Y_9Co_7 anomalies of H_{c2} are discussed The generalisation of Ginzburg-Landau theory and Abrikosov-Gorkov theory are presented The superconducting and magnetic orders in heavy fermion compounds are surveyed and models are presented The magnetism in La-214, Y-123, Bi-based and Tl-based high T_c cuprates and effect of pressure are surveyed and Heisenberg – Hubbard hamiltonian, Chakravarthy–Halperin–Nelson theory, Dyaloshinksy- Moriya interaction, RVB model, Anyon model and Spin bag model are outlined.

Keywords : Rare earth, heavy fermion and high T_c superconductors

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Plan of the Article

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6. **Other magnetic superconductors**

7. **Conclusions**

1. Introduction

Many superconductors show magnetic ordering also. They are termed as magnetic superconductors. This review aims to outline the Physics of such compounds. They may be divided into four categories : (i) Rare Earth conventional magnetic superconductors, (ii) Heavy Fermion superconductors (iii) High T_c cuprate superconductors and (iv) $(SN)_x$, $Ca_{0.5}Zn_{0.5}Fe_2O_4$ and La_2NiO_4. Section 2 gives related concepts. Each of the four types of magnetic superconductors mentioned above is discussed in separate sections (Sections 3–6).

2. Related concepts

2.1. The co-existence of superconductivity and magnetism :

The types of magnetism that are relevant to these compounds are : diamagnetism, paramagnetism, spiral (or helical or sinusoidal) order, ferromagnetism and antiferromagnetism [1].

Superconductor is a material that exhibits zero resistance and Meissner effect. The temperature below which the material behaves as superconductor is called transition temperature denoted as T_c Ginzburg-Landau theory explains superconductivity by writing the free energy density interms of powers of an order parameter, in a phenomenological way. But, the well-acclaimed theory of Bardeen–Cooper–Schriffer (BCS) focusses on phonon-mediated attractive interaction between two electrons (called Cooper pair) in the vicinity of the Fermi surface [2]. The currently known superconductors are of six classes [3]: (a) Free electron-like (*s–p* and lower *d* band) metals, (b) Strong-coupling superconductors such as Nb_3Sn and $PbMo_6S_8$, (c) Organic superconductors including doped fullerenes such as Rb_xC_{60}, (d) Heavy fermion superconductors, (e) $BaBiO_3$-based superconductors and (f) High T_c cuprates.

It is now well established that magnetism co-exists with superconductivity (SC) as below.

(i) Antiferromagnetic [AFM] ordering can exist in many superconductors because periodicity of AFM order << SC coherence length.

(ii) Ferromagnetic [FM] ordering is present in relatively less number of superconductors because of the following constraints :

FM can co-exist with SC only if :

(a) Periodicity of FM order >> SC coherence length

(b) Periodicity of FM order < SC London depth

(c) $T_m > T_c$

(d) $1 < U.N_f(0)$

where U is Coulomb-repulsion within Bose-condensate.

Spiral magnetic state can co-exist with SC state in a narrow temperature region equal to

$$T = [F_{FM}/F_{SC}]^{1/2} . T_{c2} \tag{1}$$

where F stands for free energy in the respective ordering and T_{c2} is nearly equal to T_m at which FM sets in.

Recently, researchers of China reported the co-existence of paramagnetism with SC state in a magnetic field, as will be seen in Section 5.2.

Quantum Mechanics also allows for the co-existence of SC and magnetic orderings because SC is due to phase symmetry and magnetism is due to spin symmetry and so these independent symmetries can co-exist.

2.2. Elements and phenomenae related to magnetic superconductors :

(a) The elements :

The elements relevant to magnetic superconductors in periodic table are transition elements, lanthanides and actinides. Figure 1 shows a rearrangement of d and f band elements as per

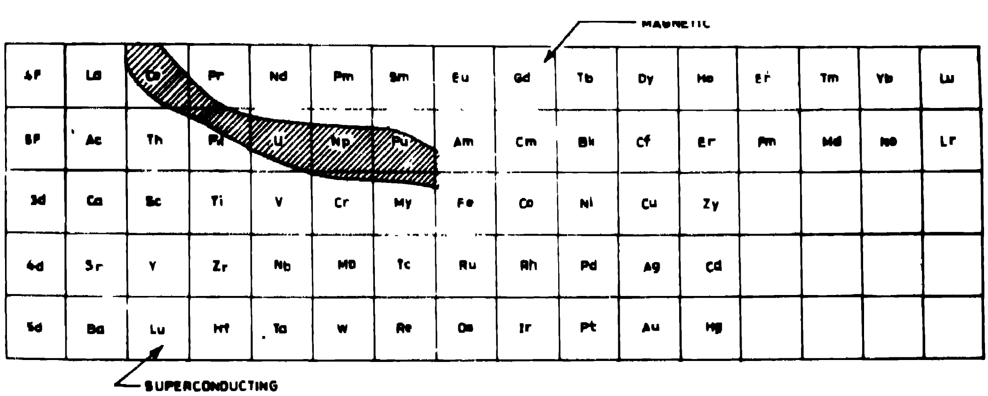

Figure 1. Rearrangement of f and d band elements as per localisation (adapted from [12]).

onset of localisation [4]. In this figure, the hatched region is the principal diagonal and contains four elements *viz :* Ce, U, Np, Pu. The cross over from itinerancy to localisation gives rise to polymorphism, spin fluctuations, mixed valences, charge density waves, kondo lattice and Heavy fermions. Hubbard model gives a magnetic phase diagram as shown in Figure 2 [5]. Here U is Coulomb repulsion between electrons and W is the band width. When pressure is applied, the elements condense into solid state. As pressure increases, the ratio U/W decreases. Figure 3 shows the variation of magnetic moment, and the ordering

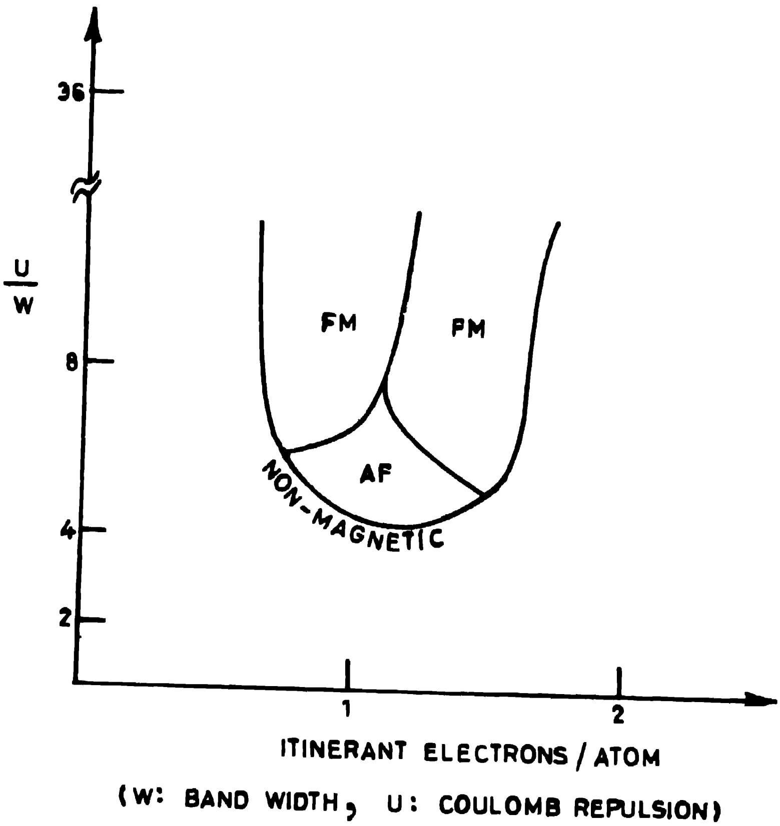

Figure 2. Hubbard magnetic phase diagram (adapted from [5]).

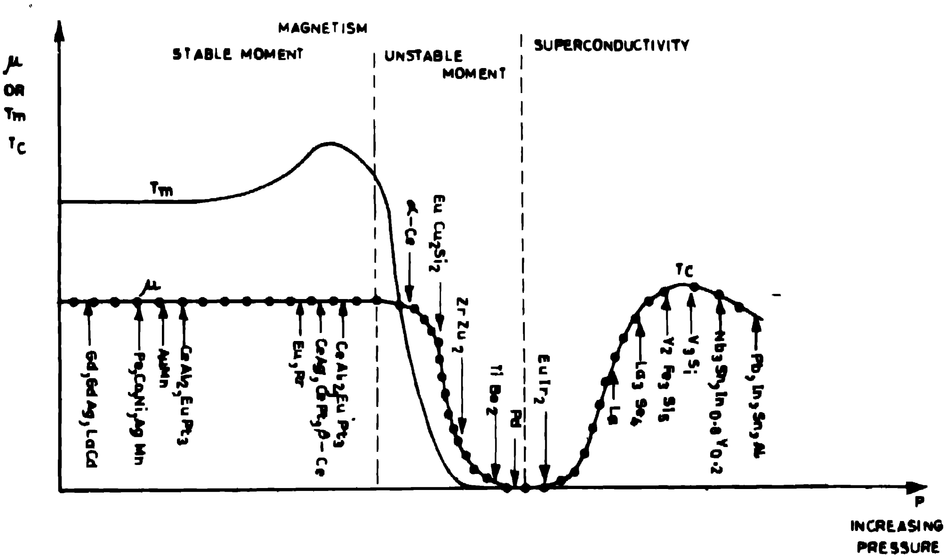

Figure 3. Magnetic moment and SC / magnetic ordering temperatures under pressure (adapted from [6]).

temperatures of magnetism and SC as functions of pressure [6]. Thus, for SC to be favoured, magnetism should disappear.

(b) Some phenomena related to magnetic superconductors :

(i) Rudderman-Kittel–Kasuya-Yoshida (RKKY) interaction :

In rare earths, the unified $4f$ shell is responsible for magnetism. However, the $4f$ electrons are deep inside the atom. So, the RE ion's localised moment spin at site 'i': S_i will interact with conduction electrons of spin s with Hamiltonian

$$H = -2J\ S_i.s \tag{2}$$

where $(-2J)$ is the exchange interaction parameter [7–9].

(ii) Kondo interaction :

If J_{sd} is the $s–d$ exchange integral, a characteristic temperature T_k exists given by the following expression :

$$T_k = E_f \exp\left[-1/\{J_{sd} \times N_f(0)\}\right] \tag{3}$$

where E_f is fermi energy and $N_f(0)$ is the density of states near fermi surface. If $J_{sd} < 0$, then there exists an AFM coupling at T_k and if $T < T_k$, there exists a bound state of electrons with binding energy $(K_B.T_K)$ and the system becomes superconducting.

(iii) Charge density waves and spin density waves :

Peierls [10] suggested in 1955 that in a one-dimensional metal, even small electron-phonon interactions will lead to lattice distortion *i.e.*, crystal field splittings and hence a charge density wave (CDW) will result. Later, Overhauser [11] observed that at low temperatures, electron-electron-electron interactions can produce a spin modulation spin density wave (SDW). Both CDW and SDW will create a gap at the fermi level and hence changes the metal to an insulator [12]. Frohlich argued [13] that the transitional motion of the CDW or SDW give rise to electric current and even superconductivity. SDW and superconductivity co-exist in HFSCs, while CDW and superconductivity co-exist in organic SCs.

(iv) Fermi liquid :

At low temperatures, a metal has the properties of a fermi liquid and the interactions between its quasi-particles governed by Landau parameters give rise to CDW or SDW or superconductivity.

(v) Migdal-Luttinger liquid :

In strongly correlated electron systems, the momentum distribution in k-space is either smeared about k_f or spread over k_f with a finite discontinuity determined by quasi-particle strength [14–16].

(vi) Mott insulator :

In periodic solids, valence electrons tend to become itinerant by hopping from atom to atom so as to lower their kinetic energy. According to Mott [17], in strongly correlated electron systems, the hopping will be opposed by Coulomb repulsion between electrons resulting in a metal–to–insulator transition and an AFM state due to localisation. Examples of Mott insulators are NiO and $YBa_2Cu_3O_6$ [18].

3. Rare earth compounds as magnetic superconductors (RESCs)

3.1. Survey of superconducting and magnetic orders in RESCs :

Ginzburg first considered whether SC and FM could co-exist [19]. Matthias *et al* [20-22] first studied the problem experimentaly. He investigated $Y_{(1-x)}Gd_xOs_2$ and $La_{(1-x)}Gd_x$ alloys and concluded that :

(i) SC is destroyed not only by FM ordering but also by small (0.1 atomic %) amounts of PM impurities.

(ii) depression of T_c should be correlated with total spin rather than the magnetic moment of paramagnetic RE impurities. He could not make any definite conclusion about co-existence of the SC and magnetic orderings because of clustering and/or formation of 'glassy' types of magnetic order. This spin glass state is characterised by short-range order and possesses a greater rigidity of spin system with respect to external magnetic field.

It was observed for the first time by Steiner *et al* [23] that superconductivity and magnetic order co-exist in the alloy $La_{(1-x)}Eu_x$. He detected that the splitting of Mossabauer line of nucleus Eu–151 vanished at a magnetic ordering temperature which is much lower than T_c. However, he could not conclude whether that magnetic ordering was FM or AFM. Roth *et al* [24] detected that FM ordering co-exists with SC order in $Ce_{(1-x)}Tb_xRu_2$ for $x = 0.2$. During 1977 Fertig *et al* [25] and Ishikawa and Fisher [26] discovered that RE ternaries $(RE)_xMo_6X_8$ where X is chalcogen and (RE) Rh_4B_4 show SC as well as magnetic orders. These are called Chevrel compounds. Baltensperger and Strassler [27] first studied the inter-play between SC and antiferromagnetism and concluded that SC state is modified by AFM order due to the pairing of electrons with finite momentum. Gorkov and Rusinov [28] first predicted co-existence of SC and FM orders. Anderson and Suhl [29] first predicted the existence of a spiral state called crypto-ferromagnetic state in these compounds. Tachiki *et al* [30,31] and Kuper *et al* [32] independently suggested that the periodic magnetic structure is due to spontaneous (self-induced) vortex (flux) states.

(i) RE Ternaries as AFMSCs and FMSCs :

$Ce_{(1-x)}M_xRu_2$ where M is Ho or Tb possess magnetic as well as SC phases. Magnetic superconducting ternaries of Pr, Nd, Sm, Tb, Dy are shown in Table 1.

Table 1. Rare earth magnetic superconductors.

S. No.	Compound	T_c (K)	T_m (K)	Magnetic order
1.	$PrMo_6S_8$	3.5	0.05	AFM
2.	$NdMo_6S_8$	3.3	0.85	AFM
3	$GdMo_6S_8$	1.1	0.85	AFM
4.	$DyMo_6S_8$	2.05	0.4	AFM
5.	$TbMo_6S_8$	1.45	0 9	AFM
6.	$Tb_2Mo_3Si_4$	0.8	19	AFM
7.	$NdRh_4B_4$	5.36	1.55	AFM
8.	$SmRh_4B_4$	2.51	0 87	AFM
9	$TmRh_4B_4$	9.8	0.4	FM
10.	$Dy(Rh_{0.85}Ru_{0.15})_4B_4$	4.0	1.5	FM

Table 2. Re–entrant magnetic superconductors.

S No	Compound	Ordering Temp	Order
1	$Dy_{1.2}Mo_6S_8$	1.7 (T_c)	SC
		0.4 (T_N)	Re–entrant AFM
2.	$HoMo_6S_8$	$T > 1.82$	PM
		1.82 to 0 7	SC
		0.71 to 0 61	SC and oscillatory state with hystersis
		$T < 0\ 612$	Long range FM
		0.668	SC only
3.	$ErMo_6S_8$	– – – –	AFM under 250 Oe
4.	$Er_{1.2}Mo_6S_8$	2.1	SC
		0.16	Re–entrant SC under H > 800 Oe
5.	$ErRh_{1.1}Sn_{3.6}$	0.46	FM, re–entrant SC
6.	$ErRh_4B_4$	8.7	SC
		1 and 0.9	Oscillatory with hystersis of SC in one branch while cooling and FM in another branch while heating the sample
		$T < 0.9$	FM only
	$Er_{0.4}Ho_{0.6}Rh_{0.4}B_{0.4}$		Re–entrant FMSC

(ii) Re-entrant RE magnetic superconductors :

Compounds shown in Table 2 show re-entrant phenomenon which may be defined as follows. They undergo a transition from normal to SC state and again become normal at a lower temperature, but now with a resistivity different from the original value. This is due to onset of long-range FM ordering or their RE magnetic moments. The transition from to SC to FM state is 1st ordered. Relative to the paramagnetic normal state, the decrease in free energy in FM state is of order of $cN\,(K_B T_m)$ where c is atomic fraction of magnetic ions and N is total number of atoms. FM state will be favoured over SC state. However, SC and FM will be co-existing just below T_{curie} because of sharp peaks in specific heat at this temperature. Moreover, the low value of magnetic moment in $ErRh_4B_4$ compared to its free ion value suggests crystal field effects or screening by conduction electrons.

(iii) Weak itinerant ferromagnetic superconductor Y_9Co_7:

The binary compound Y_9Co_7 is peculiar because it is very weak itinerant ferromagnetic superconductor below T_m= 6 K and only superconducting below T_c= 2.5 K. If pressure is applied and increased, then the value of T_m decreases and that T_c increases. At 20 kbar, ferromagnetism gets suppressed and any reentrant SC order is absent. Only the *d* electrons forming conduction band contribute to both SC and magnetism. Above T_{curie} = 4.5 K it obeys Curie-Weiss law. Steiner *et al* [33] carried out ESCA (Electron Spectroscopy for Chemical Analysis) investigations of relevant core levels and valence bands of this compound and reported that there is stronger localisation of *d* electrons in Y_9Co_7 than in metallic Co and density of *d* states at Fermi level gets enhanced.

(iv) Anomalies in the values of H_{c2}:

The AFMSCs RMo_6S_8 and RRh_4B_4 exhibit anamolies in the values of H_{c2} as follows : (a) when R = Tb, Gd, there exists a maximum in H_{c2}; (b) when R = Dy, there is a drop in H_{c2} near T_N; (c) for $NdRh_4B_4$, H_{c2} decreases at T_{N1} = 1.31 K and H_{c1} increases at T_{N2}= 0.89 K.; (d) for $TmRh_4B_4$, there is no change in H_{c2} at T_N and (e) for $ErMo_6S_8$, H_{c2} increases below T_N. Similar anomalies exist in FMSCs also. These anomalies indicate electromagnetic interaction between the persistent supercurrent and magnetic moments of REs. Ginzburg-Landau theory generalised to magnetic SCs is considered again [34].

$$f_s = \left(\frac{1}{2}\right)\alpha|\psi|^2 + \left(\frac{1}{4}\right)\beta|\psi|^4 + \left(\frac{1}{2m}\right)\left|\left(\frac{h}{i} - 2eA\right)\right|^2 + \left(\frac{1}{2}\right)\mu_0 H^2. \quad (4)$$

$$\partial f_s / \partial\psi = 0, \quad (5)$$

$$\alpha\psi + \beta|\psi|^2 + \frac{1}{2m}\left(\frac{\hbar}{i\nabla} - 2eA\right) = 0. \quad (6)$$

At H_{c2}, the SC order gets destroyed. Hence, the SC order parameter tends to vanish. This leaves the above equation as linearised as below.

$$(1/2m)\left(\frac{\hbar}{i\nabla} - 2eA\right) = 0. \quad (7)$$

This equation is equivalent to Schrodinger equation for a free electron in a magnetic field. The value H_{c2} is the maximum field for which this has a solution. It corresponds to the lowest eigen function of corresponding harmonic oscillator problem.

$$H_{c2} = m\,|\alpha|\,/\,(e\,\hbar) = \phi_0\,/\,2\pi\xi^2. \quad (8)$$

For conventional superconductor Nb : H_{c2} = 0.26 T, ξ = 360 Å; for RE magnetic superconductor $PbMo_6S_8$: H_{c2} = 60 T, ξ =23 Å.

Taking the spin polarisation into account, one has to add the term $1/2\, M^2\, \psi^2$ to free energy density f_2.

$$H_{c2}^{*} = H_{c2} - (m\gamma M^2)\,/\,(e\hbar), \quad (9)$$

where * indicates that the field is modified. So, the field gets reduced by an amount proportional to M^2, especially in the case of FMSCs. In FMSCs,

$$T_m = (4\pi\, n\, p^2 \mu_B^2)/2K_B, \quad (10)$$

where n is density of RE ions and p is effective Bohr magneton number. Since the value of p is high (9.59 for Er and 10.6 for Ho), $T_m > T_c$. This formula gives values of T_m as 2.3 K and 1.1 K for $ErRh_4B_4$ and $HoMo_6S_8$ respectively [35].

3.2. *Ginzburg–Landau theory and Abrikosov–Gorkov theory applied to conventional magnetic superconductors :*

The RESCs surveyed in Section 3.1 above can be termed as conventional magnetic superconductors because they are well explained by the Ginzburg–Landau phenomenological theory and the Arbikosov–Gorkov microscopic theory.

(i) Ginzburg-Landau (GL) theory generalised to superconducting and magnetic orders :

Das [36] extended the GL theory as below :

Case 1. Absence of magnetic field

If F stands for free energy, ψ for SC order parameter ordering to T_c and Φ for magnetic order parameter ordering at T_m or at T_N, then

$$F_s = \alpha|\psi|^2 + \left(\frac{\beta}{2}\right)|\psi|^4 + \gamma|\psi|^2, \quad (11)$$

$$F_m = \alpha'|\Phi|^2 + \left(\frac{\beta'}{2}\right)|\Phi|^4 + \gamma'|\Phi|^2, \quad (12)$$

$$F_I = \eta|\psi|^2 + |\Phi|^2 \quad (13)$$

where the subscripts s, m, and I stand for SC state, magnetic state and interaction between the two states respectively and α, β, γ, α', β', γ', and η are called GL coefficients. There are two sub-cases.

(a) When ψ and Φ are spatially uniform :

There will be no fluctuations in either parameter. By minimising the free energy F with respect to ψ and Φ one after the other, one gets the following results : If $\eta < 4\beta\beta'$, then there will be a second order phase transition from SC state to mixed state first and then another second order transition from mixed to magnetic state. If $\eta > 4\beta\beta'$, then there will be only a first order transition from SC state to magnetic state.

(b) When ψ is uniform but Φ varies spatially :

Then, there will be magnetic fluctuations and is taken to be the magnetisation M. For SC state to be favoured, M should vary spirally about some direction so that total magnetic moment is zero. Figure 4 plots the different in free energy between various states as a function of temperatures and defines the ordering temperatures T_{spiral}, T_m, and T_c where the respective

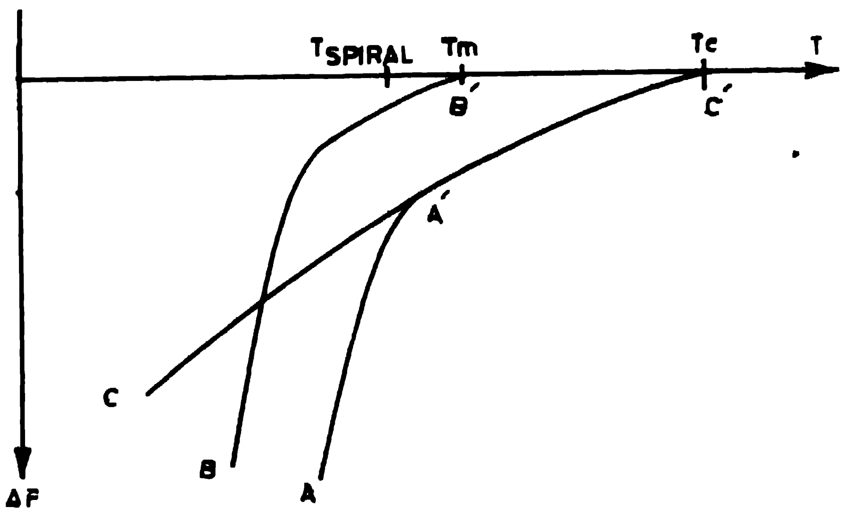

Figure 4. Difference in free energy of various orderings *versus* temperature as per generalised Ginzburg-Landau theory (adapted from [36]) (AA′ : spiral state, BB′ : magnetic state, CC′ : superconducting state)

orderings set in. The transition from SC to spiral state is 2nd order and that from spiral to ferromagnetic state is 1st order.

Case 2. Presence of magnetic field :

In this case, for negative values of η, the coherence length and H_{c1} decrease whereas London depth and H_{c2} increase when compared to the values obtained from conventional GL theory.

(ii) Abrikòsov-Gorkov (AG) theory :

The AG theory was put forward in 1961. A term for the exchange interaction between conduction electron spin and impurity spin S_i at site r_i added to BCS hamiltonian for dilute alloys containing magnetic impurities [37].

$$H = H_{BCS} + H_{cf} \tag{14}$$

where $H_{cf} \doteq J_{sf} / (2N) \sum (S_i \sigma)\, C_k^{+} C_{k'} \exp\, [i(k - k').r_i].$

The Born approximation is used for the scattering of electron on impurity. The life-time of cooper pair becomes finite. This leads to energy smearing within the gap. The result of this theory is the following expression for depression of T_c:

$$dT_c / dn_I = [-\pi^2 N_f(0) J_{sf}^2 (g_J - 1)^2 J(J+1)] / (2K_B) \tag{15}$$

$$\ln\,(T_c / T_{co}) = \psi\left(\frac{1}{2}\right) - \psi\left[(2\pi\, T_c \tau_s)^{-1} + \frac{1}{2}\right] \tag{16}$$

where $1/\tau_s = 2\pi n_I N_f(0).\, J_{sf}^2 (g_J - 1)^2 . J(J+1).$

The expression for $\ln\,(T_c / T_{co})$ can also be written as :

$$\ln(T_c / T_{co}) = \psi\left(\frac{1}{2}\right) - \psi\left[\frac{1}{2} + \beta(2T_c / T_{co})\right] \tag{17}$$

where τ_s is the mean time between exchange scattering of electron on impurity atoms, J is the total angular momentum of RE^{3+} Hund's rule ground state, n_I is impurity concentration and ψ is digamma function, T_{co} is T_c with $n_I = 0$ and g is Lande's g–factor and $[(g_J-1)^2 J(J+1)]$ is called de Gennes factor. The second expression for $\ln\,(T_c/T_{co})$ is valid in two cases as below :

Case 1 : If paramagnetic impurities are considered, the expression for β reads as :

$$\beta = (n_I / 4K_B T_{co}) N_f (2J_{sf})^2 J(J+1), \tag{18}$$

where T_{co} is the value for zero-impurity.

Case 2 : If the critical magnetic field H_{c2} which also destroys superconductivity is being considered, the expression for β reads as :

$$\beta = \left(v_f^2\, e\tau / 3\pi T_{co}\right) H_c, \tag{19}$$

where V_f is fermi velocity, e is electron charge, and τ is transport relaxation time. For heavy REs, the T_c of (RE) Rh_4B_4 and rate of depression of T_c for $LuRh_4B_4$ upon dilute substitution for Lu by these REs both vary linearly with the de Genes factor.

Tkaczkyk [38] carried out spin polarised tunneling into the side of an Al film covered with a sub-monolayer of Gd. It revealed the presence of localised RKKY spin polarisation in the normal state and its absence in the superconducting state. This is due the vanishing of the long-range part of the spin susceptibility at low temperature. The s–f exchange constant is derived from Zeeman splitting of superconducting density of states and its value agrees with that obtained from AG theory.

(iii) Modification due to interaction between conduction and f electrons

There is a limit called Clogston-Chandrasekhar limit to the exchange integral above which the superconductivity is destroyed due to spin-flip of electron of cooper pairs by electron-magnon interaction. Considering the spin-dependent interaction between the conduction electrons and magnetic electrons as well as the exchange interaction between spin of magnetic atoms, the following expression can be obtained for $\hbar\omega_{\text{phonon}} \gg K_B T_c$ and $\hbar\omega_{\text{magnon}} \gg K_B T_c$ [37].

$$\ln (T_c / T_{co}) = \psi\left(\frac{1}{2}\right) - \text{Re}\,\psi\left[\frac{2\pi}{2} + iJ_{sf}\ 1/2\pi\ T_c\right]. \tag{20}$$

Figure 5 shows a plot of $d(T_c/T_{co})/dx$ against $x = J/\Delta_0$. There are two transition temperatures T_{c1} and $T_{c2}(T_m)$. The material becomes SC with one phase transition for $x < x_2$

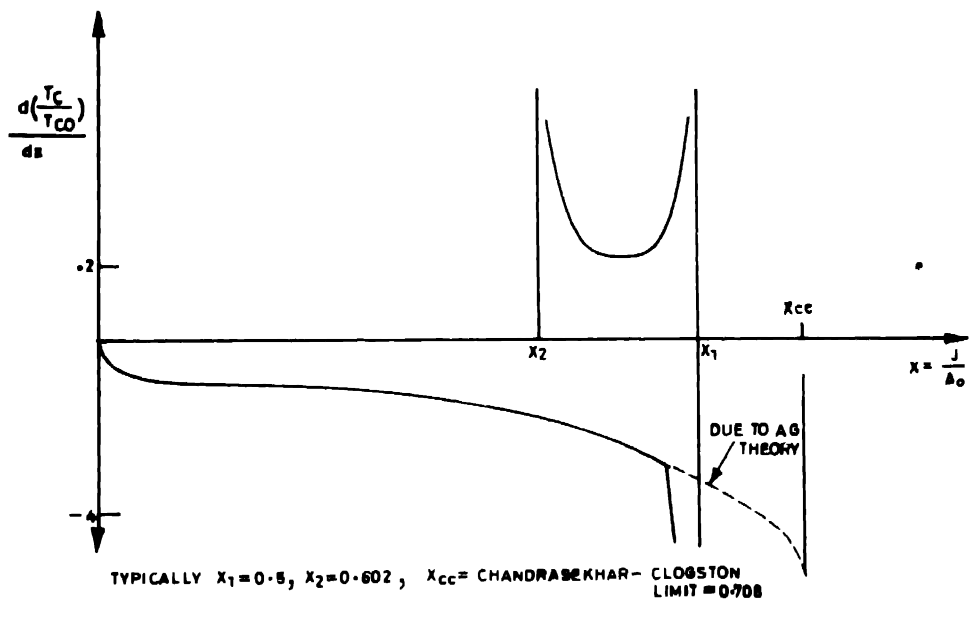

Figure 5. T_c or T_m *versus* = X for λ_{Magnon} = 0 (adapted from [37]).

and for the case of $x_1 > x > x_2$ (*i.e.*, for $J_1 > J > J_2$), this theory predicted a re-entrant behaviour. When the Kondo effect is also considered, one gets

$$\ln (n_I)\ \text{critical} = n / \left[2\pi^2 N_f(0) T_{co}\right]. \tag{21}$$

Thus, the results of the theory are : (a) For temperatures greater than T_{c1}, the material is normal. (b) For temperatures between T_{c1} and T_{c2}, it is superconducting, (c) For temperatures between T_{c2} and T_m, there is an oscillatory state. (d) Finally, for temperatures below T_m, the cooper pairs are broken and material becomes magnetic. Figure 6 depicts the phase diagram for the conventional magnetic superconductors (*i.e.*, RESCs). In this figure, line 1 represents the influence of paramagnetic ions on superconductivity. Line 2 shows the

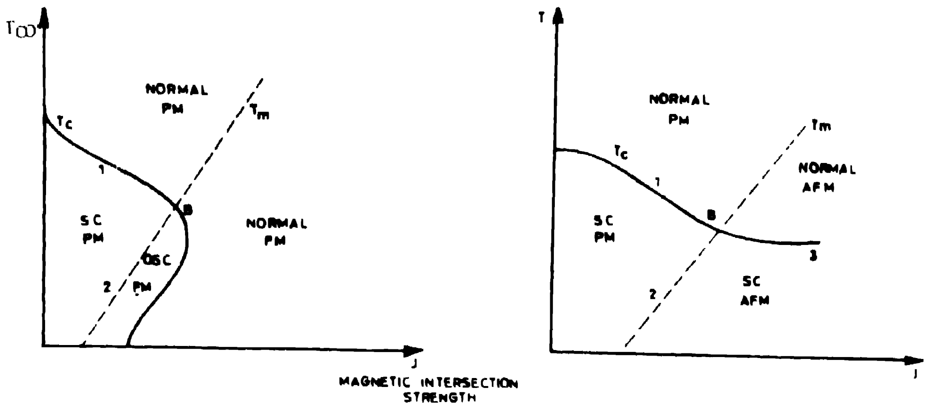

Figure 6. Phase diagram for conventional magnetic super conductors (adapted from [155]).

change in magnetic ordering temperature due to superconductivity, Line 3 represents : AFM versus superconductivity. Near point B, close to line 2, order parameters of superconductivity and magnetism are small.

(iv) Electronic specific heat of RESCs :

In AFMSCs, the electronic part of specific heat C_e shows lambda type anomaly at T_N in addition to a jump at T_c and in FMSCs, there is a jump at T_c which is superimposed on Schottky anomaly, in addition to a spike at T_{c2}. Panigrahi *et al* [39] considered AFMSC as a system of localised $4f$ electrons of RE ions and superconducting $4d$ electrons of transition metal atoms interacting with each other via an exchange interaction. By calculating thermodynamic potentials, they obtained an expression as below :

$$(C_s - C_n)_{Tc} = \left[8\pi^2 N_f(0) K_B^2 T_c / 7\xi(3)\right] = 1.42 \tag{22}$$

where $\xi(3)$ is the third order zeta function which is the same as the well-known BCS result.

4. Heavy fermion systems as magnetic superconductors

4.1. Survey of superconducting and magnetic orders in HFSCs

In metals or any other electrically conducting systems, one can write the specific heat at low temperatures as

$$C = \gamma T + \beta T^3 + \delta T^3 \ln T \tag{23}$$

where the first term γT is due to free electrons and the other two terms are due to lattice (*i.e.* phonons). The linear coefficient γ is given by :

$$\gamma = \left(m^* K_{\text{fermi}} K_B^2\right) / 3^2 h^2 \pi^2 \tag{24}$$

where symbols have usual meaning. For normal metals, its value is 0.6 mJ/mole/k^2. But for certain materials most of which contain U or Ce or Np, the value of γ is very large of the order of 1600 mJ/mole/k^2. This is due to mass enhancement of electrons which leads to large density of states at fermi level, low fermi energy, large jump in specific heat, low T_c, large magnetic susceptibility. They are called Heavy fermion compounds. The heavy mass of electron is due to an interplay between the magnetic interactions *viz* : (a) RKKY interaction where itinerant electrons mediate a ferro or antiferromagnetic polarization of magnetic moments and (b) Kondo interaction which favors a neutralization of magnetic moments by conduction electrons. de Haas-van Alphen effect proves that all of conduction electrons become heavy.

At low temperature, there are two ways in which f electron magnetic moments behave : either they order spontaneously in FM or AFM structures or the f electrons form a heavy fermion state strongly correlated with conduction electrons because of the hybridisation. Some of these materials change their ground state again, but now to an unconventional superconducting state in either of the two ways : (a) the embedding system becomes superconducting while RE ions retain their magnetic moments; (b) the f-electrons themselves form non-cooper pairs. Delong [40] observed that, if the exchange enhancement ratio R is defined by

$$R = \text{Lim}_{(T\to 0 \text{ or } T\to T_c)}\left\{(1/3)[\pi K_B / \mu^* B]^2 (\chi^* / \gamma^*)\right. \tag{25}$$

where linear specific heat coefficient γ^* (given in erg/cm^3-k^2), then the heavy fermion system is : (a) magnetic if $\gamma > 3.5 \times 10^4$, (b) non-superconductor if $3.5 \times 10^4 \le \gamma \le 10^5$, (c) superconductor if $\gamma \ge 10^5$, (d) superconductor if $R \le R_{\text{critical}} \le 4$, (e) localised Fermi liquid if $R \le 10$, (f) ferromagnetic if R diverges and (g) antiferromagnetic if R need not be large. For heavy fermion systems, there exists a characteristic temperature scale $T^* = 10 - 100$ K. When $T \ll T^*$, the magnetic susceptibility will be Pauli-like *i.e.*, independent of temperature [41] There are four types of compounds into which the heavy fermion systems can be categorised as given in Table 3. In HFSCs, SC and AFM can co-exist. A transition to either ordered state may be followed by another transition to a phase containing both states. Thus, in both UPt_3, URu_2Si_2 the transition to AFM is followed by a transition to SC state. But, in $U_{0.97}Th_{0.03}Be_{13}$, the order of transitions is reversed. $CeCu_2Si_2$ was found in 1979 by Steglich *et al* [42] and UPt_3 in 1984 by Stewart *et al* [43]. Lin discovered magnetic-field induced superconductivity in $CePb_3$. Recently, Geibel [44] discovered in 1991 that UNi_2Al_3 is a HFSC with the U–U separation equal to 4.018 Å. All heavy fermion systems contain one of Ce, U, Np and Yb with cation–cation separation greater than 4 Å. $CeIn_3$ has local moment, $CePb_3$ has heavy fermions and $CeSn_3$ is mixed–valent [45]. $CeRh_3B_2$ shows ferromagnetic ordering with T_{curie} = 120 K. (RE) Ir_2Si_2, exhibits polymorphism. When a pinch of Rh is added to URu_2Si_2, the value of T_c increased from 0.8 K to 1.65 K. Aeppli [46] found by neutron scattering technique that UPt_3 has a magnetic moment 0.02 μ_B and T_N = 5 K. Moshchalkov *et al* [47] studied anisotropy of upper critical field in URu_2Si_2. They found that the derivative (dH_{c2}/dT) is constant within 5% when H is rotated in basal plane and it decreases by about 35% for H rotated by $20^0 - 30^0$ out of basal plane. Contrary to $CeCu_2Si_2$ the H_{c2} anisotropy in URu_2Si_2 is enhanced as temperature decreases below T_c. Allen *et al* [48] reported that the compound Ce $[Ru_{(1-x)}Rh_x]_3B_2$ is superconducting if $0 < x < 0.38$ and

Table 3. Heavy fermion compounds (HFC)

S.No.	HFC–neither SC nor magnetic	Crystal structure	
1.	$CeAl_3$	Hexa (Ni_3Sn)	
2.	$CeCu_6$	Ortho	
3	YbCuAl	Monoclinic	
4	UAl_2	Cubic ($MgCu_2$)	
S No	**HFC–magnetic only**	**Magnetic order**	**Order temperature (*K*)**
1	$CeAl_2$	AFM	3.8
2	UCd_{11}	AFM	5.0
3	U_2Zn_{17}	AFM	10.0
4	$NpBe_{13}$	AFM	3.4
5	$NpIr_2$	AFM	7.5
6	$CePd_2Si_2$	AFM	10.0
7	$CeRh_2Si_2$	AFM	39.0
8	$NpOS_2$	FM	9.0
S.No.	**HFC–SC as well as AFM**	**T_N (*K*)**	**T_c (*K*)**
1	$CeCu_2Si_2$	0.7	0.6
2	UPt_3	5.0	0.5
3	URu_2Si_2	17.0	0.8
4.	UNi_2Al_3	4.6	1.0
5.	UPd_2Al_3	14.0	2.0
S.No.	**HFC–pure SC only**	**T_c (K)**	
	UBe_{13}	0.9	

exhibits ferromagnetism if $0.84 < x < 1$. FM is associated with nearly trivalent Ce ions. Pure UBe_{13} is HFSC only, without magnetic order. Kim *et al* [49] studied $U_{(1-x)}M_xBe_{13}$ for $0 \leq x \leq 0.995$ and with the non-magnetic M = Hf, Zr, Sc, Lu, Y, Pr, Ce, Th and La and found that the low-temperature magnetic susceptibility (normalized per U mole) is independent of doping for all values of x. $CeIn_3$ belongs to localised regime and $CeCu_2Si_2$ belongs to Kondo coherent regime [50].

4.2. Models of HFSCs :

All the heavy fermion systems possess strong two–body interactions *viz.* Coulombic repulsion between valence electrons which are present at sites of rare-earth ions. These cannot be explained by perturbative expansions. The quasi particles and their interactions are altered by AFM molecular field. The local repulsion of two quasi-particles at the same lattice site is reduced whereas the attraction on neighbouring sites will increase.

(i) Fermi liquid model :

The localised f electrons change from the magnetic moment regime to kondo coherent regime where the electrons form Fermi liquid quasi-particles with renormalised mass. $CeCu_2Si_2$ becomes Fermi liquid around a temperature of 1 – 2 K. The plot of specific heat versus temperature for UBe_{13} which resembles that of the conventional Fermi liquid He–3A. Norman [51] solved Eliashberg equations for UPt_3 and obtained $T_c = 0.12$ K, due to momentum dependence of susceptibility calculated with gap function having lines of zeros in parts of the zone.

(ii) Periodic Anderson lattice model (PAM) :

This model is used to explain a mixed-valence compound in which $E_{\text{Fermi}} = E_{f\text{-level}}$. In the Hamiltonian, the first term is energy of conduction band electrons, the second term is that of f–shell electrons and the third term accounts for hybridisation of f–shells with conduction band (known as c–f mixing). The results of this model are : [52]

Kondo limit of PAM is :

$$k = \left[N_f v^2 / \left(\varepsilon_f - \cdot \varepsilon_f^0\right)\right] << 1 , \tag{26}$$

$$\left(m^*/m\right) \propto \exp\left[-1/k\right] , \tag{27}$$

$$T_k \propto \mu_0^{-1/k} , \tag{28}$$

where μ_0 = chemical potential.

(iii) Kondo lattice model :

Tachiki and Maekawa [53] argued that if the HFSC is treated as consisting of independent Kondo impurities, superconductivity would not be stable owing to the dominating nature of repulsive interaction through spin fluctuations of Kondo impurities over the attractive interaction mediated by phonons and proved that :

$$C_e/C_{ec} = 1/[4 N_{Fc}(0)\, \dot{T}_k] , \tag{29}$$

where subscript F stands for Fermi and c stands for conduction electrons. The magnetic moments of RE ions disappear below T_k, forming a singlet ground state with surrounding ground state. Miyake *et al* [54] extended this model in 1984 to account for the possibility of singlet and triplet pairing leading to *d*-wave superconductivity due to AFM spin fluctuations. But in 1986, Miyake *et al* [55] concluded that AFM spin fluctuations promote neither conventional singlet superconductivity nor triplet superconductivity. They do promote anisotropic states all of which have lines of zeroes of gap on Fermi surface.

(iv) Spin density waves in HFSCs:

From the graphs of the HFSCs shown in Figure 7, it is clear that there is a close proximity between superconductivity and SDW [56].

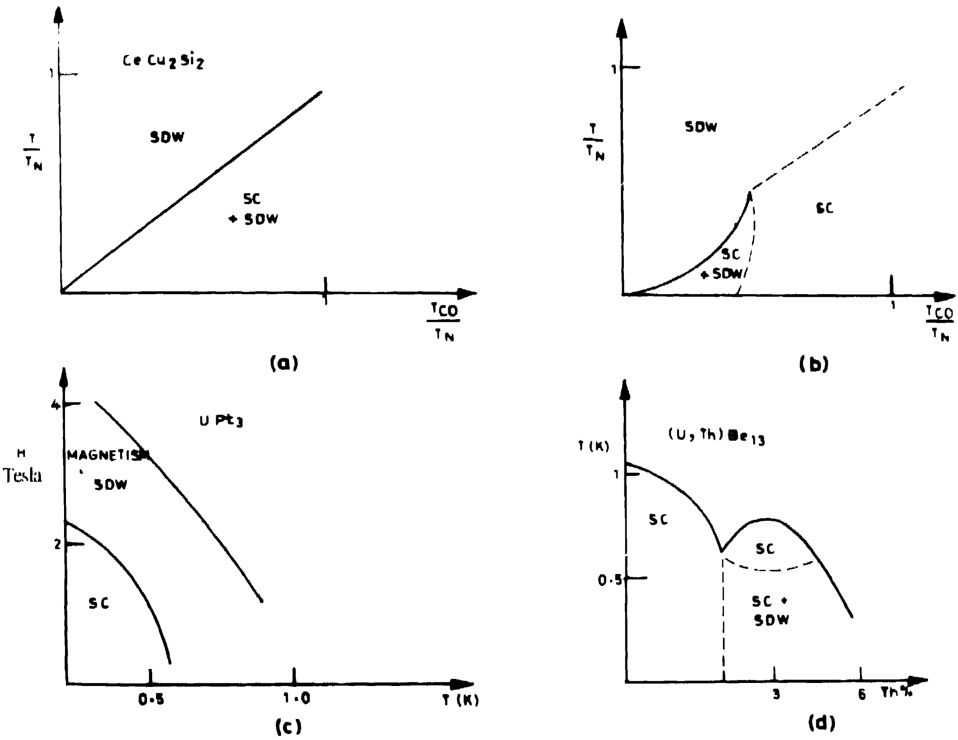

Figure 7. SDW graphs in HFSC's (adapted from [56]) (a) Generic phase diagram for *d* wave like pairing, (b) Generic phase diagram for isotropic *s*-wave pairing, (c) H–T for $CeCu_2Si_2$, (d) T–content of Th (%) in (U, Th) Be_{13}.

$$H = H_0 + H_{SDW} + H_{SC} \tag{30}$$

where

$$H_0 = \Sigma_{k\sigma}\, \varepsilon(k)\, c^+ k\sigma$$

$$H_{SDW} = -\Sigma_{k\sigma}\left(M c^+_{k+Q}\, C^+_{k\sigma} + \text{h.c.}\right)$$

$$H_{SC} = -\Sigma_{k\sigma\sigma'}\, \Delta_{\sigma\sigma'}(k)\left(c^+_{k\sigma}\, c^+_{-k\sigma} + h.c.\right)$$

where Q is SDW nesting vector and M is magnetisation.

URu_2Si_2 exhibits superconductivity with T_c = 1.5 K below a SDW transition which occurs at T_N = 17.5 K. It changes to a Fermi liquid at 60 K. In this compound, the small entropy and a BCS like jump at T_N are consistent with itinerant electron magnetism picture.

5. High T_c compounds (HTSCs) as magnetic superconductors

5.1. *Survey of superconducting and magnetic orders in HTSCs:*

Since the remarkable discovery of high T_c around 30 K by substituting a part of La in La_2CuO_4 with Ba by Bednorz and Muller [57], many superconductors with still higher values of T_c have been synthesised. All the HTSC's follow a generic phase diagram as shown in Figure 8a. As observed by Aharony *et al* [58] antiferromagnetism (AFM), insulator–metal

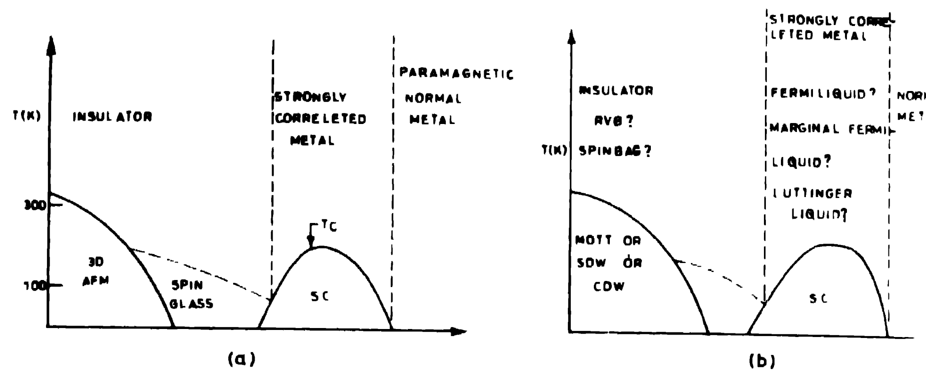

Figure 8. Generic phase diagram for HTSC's.

transition, structural transition, superconductivity are the striking features of this phase diagram. To explain these various phase, many mechanisms have been proposed as indicated in Figure 8b.

Kitaoka *et al* [59] reviewed the results of NMR and NQR on La–Sr–Cu–O, Y–Ba–Cu–O and Bi–Pb–Sr–Ca–Cu–O. The behaviour of T_1 of Cu above T_c is shown to be dominated by AF fluctuations of Cu *d* spins. In contrast, $1/T_1$ of O–17 gets enhanced just below T_c which is similar to a BCS–case.

(a) La–Sr–Cu–O system :

La_2CuO_4 exhibits three dimensional AFM ordering of Heisenberg Cu–Cu coupled Cu^{++} spins at T_N = 330 K. The undoped compound changes from tetragonal to orthorhombic at 533 K. Moncton *et al* [60] reported that the powder diffraction measurements of $La_{(2-x)}Sr_xCuO_{(4-y)}$ demonstrate the existence of superlattice peaks at temperatures below those corresponding to the maximum susceptibility and polarised neutron measurements confirm that these peaks are indeed of magnetic origin. The deduced AFM structure in orthorhombic phase consists of FM sheets of Cu atoms in the *b–c* plane which are alternating in sign along *a*–axis (100). The moment is parallel to the *c*–axis. T_N depends on *y* and decreases rapidly to zero as *y* decreases from 0.03 to 0. The saturated magnetic moment is 0.4 μ_B per Cu atom for samples with highest T_N = 290 K. La_2CuO_4 is an insulator with $N(E_F)$ = 2 states per eV per formula unit. Its low dimensionality is confirmed by the anisotropy of H_{c2} and also by the fact that substitution of La^{3+} ions by magnetic rare-earth ions has no effect on superconductivity. However, it shows Curie–Weiss behaviour above Neel point, rather it shown enhanced Pauli paramagnetism. Such absence of local moment in Sr–doped La_2CuO_4 is essential to the appearance of superconductivity. The absence of long range magnetism is a consequence of the strong hybridisation between $3d$ orbitals of Cu and $2p$ orbitals of O. There is no appreciable change in susceptibility at the transition of La_2CuO_4 from tetragonal to orthorhombic. Thio *et al* [61] found that if magnetic field is applied in the direction parallel to the Cu–O plane $\chi(T)$ does not have significant temperature dependence. However, when magnetic field is applied in the orthogonal direction then susceptibility develops peak at the T_N as shown in Figure 9. The expression $\chi = (g\mu_B)^2/J$ gives a value of 1.6×10^{-4} cm^3 per mole,

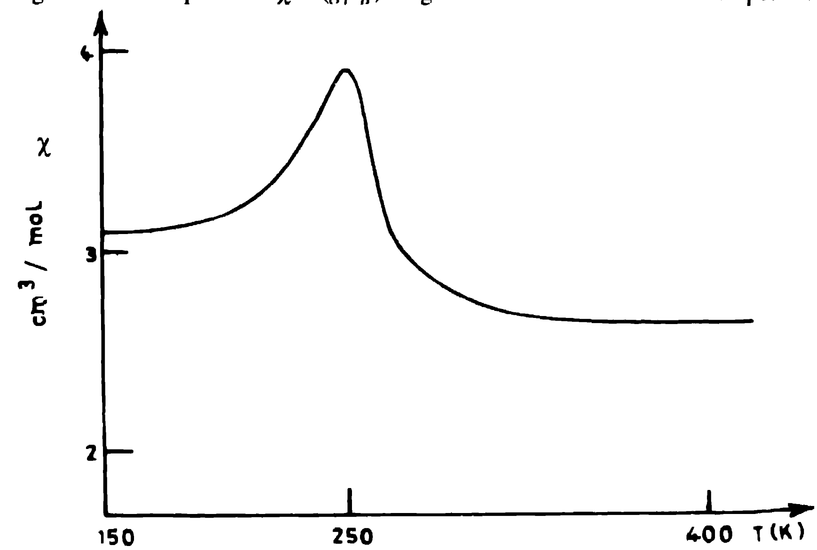

Figure 9. Magnetic susceptibility *versus* temperature for HTSC [61]

when J = 1200 K. Shinjo *et al* [62] investigated the Mossabauer absorption for Sn–119 and Fe–57 in $La_{2-x}Sr_xCuO_4$ for x = 0, 0.15, 0.4. The results indicate that the Cu magnetic spins are collectively fluctuating in the superconducting sample. Nakamura and Kumagai [63] found that $1/T_1$ of Cu–NQR, in La–Sr–Cu–O is suppressed by superconducting energy gap for $0.12 < x < 0.2$, while its temperature–dependence obeys the Korringa relation in normal region. The strong correlation between high T_c and the AFM fluctuations of Cu spins is indicated by the clear changes of enhancement of $1/T_1$ and $1/T_2$. Kitaoka *et al* [64] reported, again by Cu–NQR study of $La_{(2-x)}Sr_xCuO_4$, that as x and temperature increase, the quantity $(T_1T)^{-1}$ also increases and follows a Curie Weiss temperature-dependence associated with staggered susceptibility at zone-boundary $Q = (\pi/a, \pi/a)$. The Weiss temperature decreases from 75 K (x = 0.15) to 20 K (x = 0.075), causing the enhancement of the quantity $(T_1T)^{-1}$

and decrease of T_c. For $x = 0.05$, the Weiss temperature becomes zero and the Curie constant C slightly increase.

(b) Y–Ba–Cu–O :

Petitgrand and Collin [65] reported that when $x = 6.55$, antiferromagnetism co-exists with superconductivity in $YBa_2Cu_3O_x$. Neidermayer *et al* [66] performed muon spin resonance experiments on $YBa_2Cu_3O_7$ samples doped with hydrogen. For hydrogen concentration larger than 0.5 per formula unit, a well defined precession signal in zero external field was observed. This indicated the magnetic ordering. Hydrogen acts as an electron donor filling the hole states.

(c) (RE)–Ba–Cu–O :

For (RE) $Ba_2Cu_3O_7$, the substitution of RE atoms does not affect the T_c in a significant way (except for Gd, Pr and Tb) eventhough large magnetic moments exist for Gd, Er, Ho. This is because high T_c superconductivity is essentially quasi dimensional and is strongly confined to the Cu–O planes above and below the RE ion site. T_c strongly correlates with the size of paramagnetic moment. Vidyalal *et al* [67] studied $GdCo_xBa_2Cu_3O_7$ and found that 7.36 weight % of Co will raise the T_c from 93 K to 109.5 K and T_c decreases at higher concentration of Co impurity. These authors claim that this is for the first time the transition impurity has been found to raise the T_c for a superconducting ceramic. Changyong Sun *et al* [68] reported that magnetic RE ions *viz.*, Sm, Eu, Gd, Dy, Ho, Dr, Tm do not change the value of T_c appreciably but change the magnetic behaviour of compound. The magnetisation loops were measured at 77 K. Superconductivity co-exists with magnetic ordering when RE = Gd, Dy, Ho, Er, Tm. The magnetism of samples originates from local magnetic moments of RE ions. Lutgemeir *et al* [69] investigated the NQR spectra of Cu and Mossbauer spectra of (RE)–Ba–Cu–O. A transition from the high temperature AFM spin structure of magnetic moments at the Cu(2) sites with the stacking sequence (+ – + –) to another one at low temperature (+ + – –) is induced by a small amount (about 1%) of magnetic impurities at the Cu(1) sites. The Cu(1) ions themselves carry no magnetic moments. Del Morel *et al* [70] measured the magnetostriction and thermal expansion of (RE)–Ba–Cu–O compounds. The magnetostriction parallel and perpendicular to applied magnetic field is measured between 3.8 K upto above T_c with fields upto 2.45 T. The anisotropic magnetostriction is very weak at 4.2 K. Chattopadhay *et al* [71] performed Neutron diffraction on polycrystalline samples of $ErBa_2Cu_3O_7$ and reported that the Er moments are ordered three dimensionally at $T = 140$ mK. Two independent propagation vectors $k_1 = (1/2, 0, 0)$ and $k_2 = (1/2, 0, 1/2)$ are required to describe the magnetic reflections which indicate the existence of both FM and AFM coupling between moments along c–axis. But, Lynn *et al* [72] carried out neutron scattering experiments to study the magnetic order of Er ions and concluded that above the three dimensional Neel point $T_N = 0.618$ K, a two-dimensional magnetic order is observed. Thus, the magnetic interactions of RE ions (Er) are highly anisotropic and hence Ising AF magnet is appropriate. Lynn *et al* [73] performed neutron diffraction studies on single crystals of $NdBa_2Cu_3O_{(6+x)}$. The Cu–O planes get ordered antiferromagnetically at T_{N1} = 450 K at x = 0. These authors reported that when x = 0.1, there exists a simple antiferromagnetic sequencing along c–axis with T_{N2} = 80 K. Both T_{N1} and T_{N2} decrease as x increases with T_{N2} being much more sensitive to than T_{N1}. Fischer *et al* [74] performed powder neutron diffraction studies found that there exist magnetic Nd moments of $NdBa_2Cu_3O_{6.86}$ (T_c = 88 K) ordered in 3–D AFM configuration below T_N = (551 ± 10) mK with wavevector K = [1/2, 1/2, 1/2] as in similar Gd and Dy compounds and with u_{sat} = 1.14 ± 0.06 μ_B. At 25 mK, the magnetic moments and oriented parallel to (0, 0, 1). The transition to the magnetically ordered state corresponds to the Landau–type critical exponent I = 0.5 in contrast to the predominant 2D character of such heavy rare-earth systems. Mook *et al* [75] confirmed, by neutron scattering that Gd $Ba_2Cu_3O_y$ possesses magnetic ordering for y = 6.14. Kuno *et al* [76] investigated $HoBa_2Cu_3O_y$ using the zero field muon spin resonance technique and observed a long range magnetic of Cu moments in the tetragonal insulting phase. At T < 3 K, freezing of Ho magnetic moment was observed in 90 K–superconductor with y = 6.9. Thus, the effect of the magnetic rare-earth ion Ho^{3+} on antiferromagnetism of Cu ions is small. Gang Xiao *et al* [77] reported that the initial susceptibility of Gd_2CuO_4 and $Gd_{1.85}Sr_{0.15}CuO_4$ indicates a Neel state in the CuO_2 plane at T_N = 285 K and another magnetic transition at low temperature.

(d) HTSCs derived from Y–Ba–Cu–O by substituting Cu with Fe, Co, Mn, Ni or Zn :

Nakamichi *et al* [78] performed the NMR experiments of $YBa_2[Cu_{(1-x)}Fe_x]_3O_7$ and concluded that the temperature dependence of NMR rate both Cu (1) and Cu (2) sites indicates the appearance of magnetic order without destroying superconductivity. Bottyan *et al* [79] performed NQR investigations around 30 MHz and concluded that T_{N2} depends on concentration of Fe with a value 130 K for x = 0.01 Fe–57 and Co–57 Mossbauer spectroscopy at 4.2 K with and without an external field of 5T revealed that below x = 0.0015, Fe spins are developed from the Cu (2) moments in the AFM state. Bhargava *et al* [80] studied 11 compositions of $YBa_2Cu_{(3-x)}Fe_xO_{(7-y)}$. Paramagnetic spectra at ambient temperature consist of 4 components which are symmetric doublets. The magnetic splitting at low temperatures is due to the slowing down of spin relaxation frequencies and not due to any magnetic ordering of any moments, when x is low. There is no co-existence of superconducting and magnetism in these HTSCs. This is evident from the fact that the transition from symmetric paramagnetic doublet to the magnetic split spectra on lowering the temperature occurs through formation of asymmetric doublets. Tomy *et al* [81] studied $EuBa_2[Cu_{(1-x)}Zn_x]_3O_{(7-y)}$ with 0 < x < 0.1. Small amounts of Zn substituted at Cu site suppresses drastically T_c of $EuBa_2Cu_3O_{(7-y)}$. The rare-earth Eu has two valence states 2+, which carries large magnetic moment and 3+, which exhibits only Van Vleck paramagnetism. The magnetic susceptibility for each sample is close to the value expected for Eu^{3+} ions. A large peak in is observed below 40 K which may be due to either local magnetic moments on

Cu ions or due to the stabilization of a small fraction of Eu^{2+} ions. The Mossbauer studies indicated that Eu ions remain in trivalent non-magnetic valence state even after Zn substitution. Bhatia *et al* [82] reported that in annealed YBCO, variable range hopping as proposed by Mott was observed to persist upto 100 K. Doping by Al, Mg or Zn has not altered this behaviour whereas substitution by Ni does change its character. This is due to the magnetic moment of Ni. Without Co or Ni or Zn $T_c = 90$. With Zn = 5%, $T_c = 61$ K and with Zn 30%, $T_c = 47$ K and with Ni = 18%, $T_c = 57$ K.

(e) HTSCs derived from Y–Ba–Cu–O by substituting Y with Pr, Fe, Dy :

Lyubutin *et al* [83] observed superconducting transitions in $Y_{(1-x)}Fe_xBa_2Cu_3O_y$ at $x = 0.3$. In the interval values of x between 0.1 and 0.3, a magnetic ordering of the Fe atoms in the 'copper sublattice' coexists with superconductivity. Kebede *et al* [84] investigated $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ alloy. Pr–Ba–Cu–O is AFM Semiconducter with $T_N = 17$ K and Y–Ba–Cu–O is HTSC. T_c decreases as x increases as per Abrikosov–Gorkov pair breaking curve with critical concentration $x_{cr} = 0.62$. Alloying also reduces T_N approximately linearly with Y–content and there is a concentration region $0.4 < x < 0.6$ where AFM and SC are suggested to co-exist. Cooke *et al* [85] observed AFM ordering of Cu moments $[Y_{(1-x)}Pr_x]Ba_2Cu_3O_7$ using muon spin relaxation (zero field). For the values of $x = 1$, 0.8, 0.6, 0.58 and 0.54, the values of T_N are 285, 220, 35, 30 and 20 K respectively. For $x = 0.5$, there exists a fast-relaxing component and a long-time tail of muon polarisation, reminiscent of spinglass behaviour. The value of T_N for $PrBa_2Cu_3O_6 = 325$ K. Nowik *et al* [86] performed Mossbauer studies of Fe–57 in $RBa_{(2-y)}K_y[Cu_{(1-x)}Fe_x]_3O_z$ with $R = Y$ and Pr, $y = 0, 0.5$; $x = 0.01, 0.05, 0.1$; z is between 5.9 and 7.1. A minority of iron ions enter the Cu (2) site and reveal its magnetic order. (1) For $R = Y$, $y = 0$, and $x = 0.1$, the values of T_N are 280 K for $z = 6.5$ and 415 K for $z = 6.1$. (2) For R = Pr, $y = 0$, $x = 0.1$, $z = 6.9$, $T_N = 325$ K. (3) For the superconductor with $R = Y$, $y = 0$, $x = 0.1$, $z = 7.1$, there is no magnetic order. (4) For the superconductor $R = Y$, $y = 0.5$, $x = 0.05$, $z = 6.5$, $T_N = 450$ K. Ruixing Liang *et al* [87] found that when Cu in YBCO is partially substituted by Ni, the Ni ion is trivalent and with 2.4. For a given oxygen concentration, substitution of Cu by Zn always gives a steeper depression of T_c than the substitution by Ni.

(f) Other HTSC systems :

Barminger *et al* [88] studied X-ray diffraction and Mossbauer studies of Fe–57 probe in $CaLaBa[Cu_{(1-x)}Fe_x]_3O_z$. For $z = 7$, 10% of iron is magnetically ordered with $T_N = 400$ K, even though the sample is superconducting. But, for $z = 6.5$, it is non-superconducting with $T_N = 340$ K. Mizuki *et al* [89] reported, by polarized neutron diffraction measurements that $TlBa_2YCu_2O_7$ has AFM ordering of Cu sub-lattice in analogy with that of YBCO. Morrish *et al* [90] found that the decrease in T_c for $Tl_2CaBa_2[Cu_{(1-x)}Fe_x]O_{(8+y)}$ is less than that for the iron-doped 1–2–3 compounds. Kumagai *et al* [91] carried out zero-field Cu–NMR of $Nd_{2-x}Ce_xCuO_{(4-y)}$ around 60–140 MHz, which indicated that spins of Cu are antiferromagnetically ordered near the superconducting phase. Igalson [92] reported that when $y = 0$ and $x = 0.15$, this compound has the Curie–Weiss susceptibility in normal state for low external fields (5G) and shows deviations at higher fields at $T = 40$ K. Its Curie–Weiss temperature is –70 K. Suryanarayanan *et al* [93] investigated $YSrCuO_y$, which showed

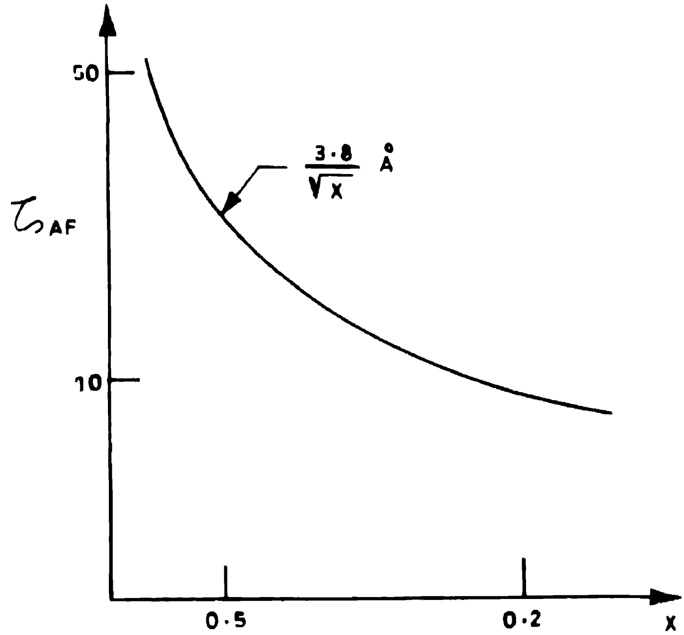

Figure 10. AFM Correlation length ζ_{AF} *versus* x for $La_{(2-x)}Sr_xCuO_4$

superconducting transition at 72 K and an AFM transition at 15 K. Luke *et al* [94] performed muon spin resonance investigations on the electron-superconductors Ln_2CuO_{4-y} where Ln = Nd, Sm, Pr and concluded that they exhibit static magnetic order below 300 K. Yang *et al* [95] studied the system $RBa_2Cu_3O_{(7-y)}$ where T = Nd and Sm whose T_c = 92 K. Their specific heat anomaly at low temperature (0.5 to 4 K) is due to magnetic ordering of Nd^{3+} and Sm^{3+} ions and can be described by a two-dimensional anisotropic antiferromagnetic Ising model. For Nd sample, the magnetic moment > 1.07 μ_B. Kumagai *et al* [96] investigated Cu-NQR spectra of $Bi_2Sr_2\left[Ca_{(1-x)}Cu_2O_{(8+y)}\right]$ and reported that the paramagnetic region of this compound is spread over a wide frequency range between 18 and 32 MHz, showing a large distribution of antiferromagnetism of Cu spins in superconducting phase. Using muon spin resonance, Sternlieb *et al* [97] concluded that another Bi-based HTSC *viz.*, $Bi_2Sr_{(3-x)}Y_xCu_2I_8$ has a value of T_c = 65 K when x = 0.3. The value of T_N decreases rapidly as x increases. Tarascon *et al* [98] reported that the layered oxides $Bi_2(SrCa)_2MnO_{(6+y)}$ or $Bi_2Sr_2CoO_{(6+y)}$ have anomalously sharp peaks in their magnetic susceptibility temperature dependences. This peak occurs at 120 K and 100 K for Bi–Sr–Ca–Mn–O and is strongly dependent on temperature for the Co materials, ranging from 80 K to 220 K. This sharp anomaly in χ–T is similar to that observed in La_2CuO_4, but these authors believe that its origin is different, but rather to ferromagnetism of individual MnO_2 layers. However, there is an important HTSC *viz.*, $Ba_{0.6}K_{0.4}BiO_3$ with $T_c = 30$ K in which there is no sign of magnetic moment at all.

(g) Some recent investigations :

(i) Co–existence of paramagnetism with superconductivity in (RE)–Ba–Cu–O in magnetic field :

According to Tarascon *et al* [99] and Thompson *et al* [100], T_c does not change when Y in $YBa_2Cu_3O_{(6+x)}$ was substituted by most magnetic rare-earth elements. Zhang Yuhang *et al* [101] reported at the International conference M^2–HTSC, Kanazawa that they observed paramagnetism to co–exist with superconductivity when magnetic susceptibility was measured in RBCO specimens (R = Sm, Gd, Er, Ho, Dy) at liquid nitrogen temperature 77 K upto a magnetic field of 0.25 tesla. If magnetic field is lower, the diamagnetism is more prominent but as magnetic moment increases from Sm ($\mu = 1.6\ \mu_B$) to Dy ($\mu = 10.63\ \mu_B$) and magnetic field is increased, paramagnetism appears and becomes prominent as indicated by the change in the value of susceptibility from negative to positive.

(ii) Theory for the effect of magnetic impurity Pr in YBCO :

Pr–Ba–Cu–O is non-superconductor and has high resistivity at low temperature. Pr ions have a localised magnetic moment caused by $4f$ electrons and undergo the magnetic ordering at about 15 K. In $Y_{(1-x)}Pr_xBa_2Cu_3O_7$ alloy, the substitution of Y for Pr results in an abrupt reduction in T_c vanishing at $x = 0.45$. Many factors may affect on T_c as a function of Y and Pr layer thicknesses. Serguei N Burmistrov *et al* [102] considered only the localized magnetic moments. These are layers of pure superconducting (S) and superconducting alongwith localised magnetic moments (SM) with thicknesses d_s and d_{sm} respectively. If magnetic impurity concentration n_I is more than its critical value, SM is a normal metal at zero temperature. Also $T_c > T_m$. So, any spin–spin correlation is absent because magnetic ions are disordered. Using Green's function technique, they obtained the expression for T_c as below :

$$T_c = T_{co} - (\pi/4\tau)\ [d_{sm}/(d_s + d_{sm})]\ , \tag{31}$$

where τ is called the pair-breaking parameter or spin–flip time in S–M layer. If $d_s > \xi$, then $T_c = Tco$. If $d_s = 0$, the results reduce to the case of Abrikosov–Gorkov.

(iii) Mossbauer studies of YBCO :

Muon spectroscopy and Mossbauer effect of effective hyperfinefield on substituted Fe–57 can be used to probe the magnetic orderings in HTSCs. Hodges *et al* [103] diluted Y in YBCO by 170–Yb^{3+} ($4f$ shell). This does not influence superconducting properties. The properties of static internal field were taken by Mossbauer measurements ($I_g = 0$, $I_{ex} = 20$ and $E = 84$ keV) in zero applied field within temperature range 1.4 to 90 K. The internal field acting on Yb^{3+} is a net molecular field due to exchange/dipole interactions with the magnetically ordered Cu (2) neighbours. (a) In $x = 0$ sample, the line shape corresponds to single ion paramagnetic fluctuations. (b) For $x = 6$, field = 1600 Gauss, with a Gaussian distribution of standard deviation 800 G. (c) For $x = 6.35$, field = 2100 G. (d) For x between 6.35 and 6.6, there exists a spin–glass like properties *i.e.*, co-existence of local magnetic and superconducting orderings.

(iv) Co–existence of AF and spin glass in Y-Ba-(Cu-Fe)-O :

Mirebeau *et al* [104] investigated polycrystalline sample $YBa_2[Cu_{0.88}Fe_{0.12}]_3O_{6.5}$ by means of three techniques *viz.*, neutron diffraction, quasi–elastic neutron scattering and Mossbauer effect. At this oxygen concentration, the sample is not superconducting but is semiconducting. At short neutron wavelengths, there exist a small AF Bragg peak and $T_N = 430$ K. The AF order shows a re–entrant behaviour below 70 K characterised by a slight decrease in AF intensity. However, when oxygen concentration is $y = 7.17$, the samples remain superconducting upto Fe–15% with T_c above the spin glass freezing.

(v) Fluctuation diamagnetism in HTSCs at $T > T_c$:

Kanode *et al* [105] observed for the first time that the temperature dependence of magnetic susceptibility of polycrystalline samples of $YBa_2Cu_3O_7$ exhibited a pronounced diamagnetic contribution at $T < 150$ K which increased as $T \rightarrow T_c$. Panfilov *et al* [106] showed :

$$\delta\chi_{\parallel}(T) = -\left(\frac{\pi k_B T}{6\phi_0^2}\right)\xi_{ab}(0)\left(\frac{m_c}{m_{ab}}\right)^{\frac{1}{2}}\left[\tau + \frac{d^2\tau}{4\xi_c(T)}\right]^{-\frac{1}{2}}, \tag{32}$$

where $\xi_{ab}(0)$, $\xi_c(0)$ are coherence length in ab–plane and along c–axis extrapolated to $T = 0$ K, $\tau = (m_c/m_{ab})$ is the ratio of effective masses of pairs $\zeta = (T - T_c)/T_c$, d is the separation between superconducting layers and ϕ_0 is the fluxoid

Kadowaki *et al* [107] reported that the value of fluctuation diamagnetism in $Bi_2Sr_2CaCu_2O_{(8+x)}$ (Bi–2212) single crystals is appreciably perturbed by their non-monophasic character. The region of two–dimensional fluctuations in Bi–2212 is much wider and closer to T_c than in Y–123. This indicates that Bi–2212 is more anisotropic than Y–123. It gives the Ginzburg–Landau parameter $k = \lambda_L/\xi = 0.03 - 0.05$ which determined the width of critical fluctuation region. Thus, the pronounced fluctuation diamagnetism is a universal property of HTSCs.

(vi) New phases in RE doped La–Ba–Cu–O :

Maeno *et al* [108] reported that there are two structural transitions in $La_{(2-x)}Ba_xCuO_4$ around $x = 0.125$. One is from high temperature tetragonal (HTT) (space group : 14/mmm) phase to medium temperature orthorhombic (MTO) (cmca) phase and then from MTO to low temperature orthorhombic (LTO) (p42.ncm) phase. Similarly, low temperature phase transition is observed when Sr in $La_{(2-x)}Sr_xCuO_4$ is partially replaced by Nd, Gd, Eu, Tb and

Dy but not when it is doped by Pr. Depending on Sr and Nd concentration, a new orthorhombic phase (Pccn) is also observed. Hara *et al* [109] measured magnetic susceptibility of $La_{1.875-x}R_xBa_{0.125}CuO_4$ where R = Nd or Sm down to 5 K under a magnetic field of 10 Oe using a SQUID magnetometer and found that superconductivity does not recover by Nd doping upto $x = 0.2$ and Sm upto $x = 0.1$.

(h) Effect of pressure on HTSCs :

(i) Effect of pressure of Neel point :

Susumu Katano *et al* [110] studied the effect of pressure of antiferromagnetism in $[La (Ba, Sr)]_2CuO_4$ by neutron diffraction under hydrostatic pressure upto 1.5 GPa. They found that the value of T_N increases with pressure at the rate of 18.5 k/GPa or equivalently $(1/T_N)$ $(dT_N/dP) = 0.083$/GPa whereas the ordered magnetic moment M is suppressed under pressure as $(1/M)\, dM/dP) = -0.08$/GPa. The value of T_c increases with pressure as $dT_c/dP = +4$ K/GPa whereas $(1/T_c)\,(dT_c/dP) = 0.1$/GPa. Thus, there is a correlation in the values of relative pressure derivatives of T_N and T_c.

The relative pressure derivative for T_N in the case of La–system is larger than for typical three dimensional AF magnets according to the formula known as 10/3 law [111].

$$dT_N/dP = (10/3)\ T_N/B, \tag{33}$$

where B is the bulk modulus. Lynn gave the below formula for T_N for large J/J'.

$$T_N = M^2\ J/\ln\ (J/J'), \tag{34}$$

where M is ordered magnetic moment.

In terms of the two–dimensional magnetic correlation length in units of lattice spacing, the expression for T_N reads as :

$$T_N = M^2\, J'\ \zeta_{AF}^2 \tag{35}$$

Barbara *et al* [112] investigated under high pressure $La_2Cu_{0.2}O_{4+y}$ which shows bulk SC below $T_c = 37$ K and AFM order below $T_N = 240$ K. dT_N/dP has been determined d.c. susceptibility and resistivity measurements under pressure. dT_c/dP and dT_N/dP are found to have opposite signs. This experimental result is confronted to the theory.

In Nd–system, as pressure increases, the above correlation length decreases and J' increases, thereby increasing the value of T_N. But in La–system, the effect of pressure on J' is small [110]. For Nd(Y) $Ba_2Cu_3O_7$,

$$dT_c/dP = 0.8\text{K/GPa} \quad \text{and} \quad dT_N/dP = 230\text{K/GPa}.$$

However, there are also reports that when La–system is in filamentary (non-bulk) state, increase in pressure will result in decrease of T_N.

Neumeier *et al* [113] reported that for the HTSC system $Y_{(1-x)}Pr_xBa_2Cu_3O_{(7-y)}$, the value of the derivative dT_c/dp changes sign from positive to negative between $x = 0.3$ and $x = 0.4$.

(ii) Effect of pressure on resistivity of HTSCs :

Now, a brief review of high pressure studies of the High T_c magnetic superconductors carried out at Anna University, is presented. Arumugam *et al* [114] reported that the partial substitution of Fe for Cu in the 1–2–3 compound $YBa_2Cu_3O_7$ shows structural transition from orthorhombic to tetragonal phase. But, T_c is not sensitive to the transition although the magnetic atoms like Fe are distributed in the superconducting plane rather than any other sub-lattice leading to interesting co-existence of magnetic ordering and superconductivity. For $x = 0.033$, in $YBa_2Cu_{2.91}Fe_{0.09}O_{(7-x)}$, the observed behaviour of normalised resistivity suggests possible metallization around 15 kb. In the conventional superconductors, the paramagnetic impurities strongly depress the T_c. In contrast, T_c of (RE) $Ba_2Cu_3O_{(7-x)}$ are more sensitive to the oxygen deficiency than the presence of RE ions. Arumugam *et al* [115] reported that for $HoBa_2Cu_3O_{(7-x)}$, the resistivity decreases steeply upto 30 kbar and decreases gradually upto 80 kbar. Thus, the transition from orthorhombic to tetragonal phase is around 30 kbar, rather than at 200 kbar, which was reported by Oslen *et al* [116]. Arumugam and Natarajan [117] reported that resistivity of nitrogen annealed $Y_{(1-x)}Pr_xBa_2Cu_3O_{(7-y)}$ increases with increase in pressure upto 30 kbar followed by a continuous decrease in resistivity upto 80 kbar. The resistivity of air-quenched and oxygen annealed samples steeply decreases with pressure upto 25 kbar followed by a gradual decrease in resistivity upto 80 kbar. This suggests a possible metallization around 30 kbar. T_c of $Pr_xY_{(1-x)}Ba_2Cu_3O_7$ decreases as x increases. There is a pressure induced electronic phase transition around 6 kbar for $x = 0.3$. Gd^{3+} has the highest spin among all RE ions. Pure $GdBa_2Cu_3O_7$ remains orthorhombic upto 150 kbar. Sampath Kumar *et al* [118] reported that resistivity of $Pr_{0.1}Gd_{0.9}Ba_2Cu_3O_{(7-x)}$ at room temperature decreases continuously with pressure upto 80 kbar whereas $GdBa_2Cu_3O_7$ shows a sharp drop upto 20 kbar followed by a small increase around 25 kbar. Shaji Kumar *et al* [119] reported that $La_{1.8}Bi_{0.2}Sr_{0.2}CuO_4$ shows large increase in T_c under pressure compared to YBCO system. The replacement of La by Bi in the Sr–compound also increase the T_c value. Among the RE ions, only the three $RBa_2Cu_3O_7$ with R = Ce, Pr and Tb do not exhibit super-conductivity. Arumugam *et al* [120] reported that $PrBa_2Cu_3O_{(7-x)}$ shows a sharp drop in resistivity upto 20 kbar followed by nearly a value upto 40 kbar. Above 40 kbar, there is an increase in resistivity upto 80 kbar.

5.2. *Theoretical aspects of magnetism in HTSCs :*

BCS theory could not explain the exotic properties of HTSCs such as high T_c, high London depth, low coherence length high critical field, high coupling constant, low co–efficient of isotope effect, linear dependence of resistivity on temperature in ab–plane, tunnelling conductance, Non–Korringa behaviour of NMR, appearance of AFM order at low doping and spin–glass nature at medium doping. Though many models have been proposed, only those which rely upon the appearance of magnetic ordering are presented below. Both valence considerations and band structure calculations predict that HTSCs should be metals at zero or low carrier concentration. But experimentally, it is now well established that most of them are insulators. Thus, as indicated earlier, Mott transition *via* Hubbard splitting, spin density waves (SDW) and charge density waves (CDW) have been proposed to explain the observed insulating nature. However, since $BaBiO_3$ is diamagnetic and belongs to the class of CDW insulator, it is not dealt with here. When carriers are introduced, the number of closely spaced CuO_2 layers increases and each layer contributes 1.2 – 1.5 × 10^{-3} emu/mole to the magnetic spin susceptibility. Liu Fusui [121] argued that the enhancement of phonon mediated superconductivity by antiferromagnetism by coupled atoms causes the high T_c.

(a) Spin polarised local spin density calculations :

By spin–polarised local spin density functional calculations using Linear Muffin–tin Orbital method using atomic sphere approximation, Barbara Szpunar *et al* [122] predicted that the magnetic nature of Cu sites strongly depends on the local oxygen environment and hence Cu in the CuO_x chains has no magnetic moment and Cu^{2+} of CuO_2 planes only have a local moment. Tranquada *et al* [123] have confirmed it by neutron diffraction experiments with a value of local moment of 0.48 ± 0.008 μ_B per Cu^{2+} in the conduction layer only. The AFM ordering between Cu^{2+} sited of different planes is negligible.

(b) Heisenberg Hamiltonian :

The Heisenberg spin – 1/2 Hamiltonian is :

$$H = \sum \left[J_{ij} S_i \cdot S_j \right]. \tag{36}$$

However, Choudhury [124] observes that the actual Hamiltonian to La_2CuO_4 is :

$$H = -J \sum S_i \cdot S_j + J_A \sum S_i^z S_j^z - J' \sum S_i : S_k \tag{37}$$

where J is isotropic part of intra–layer coupling, J_A is anisotropic part of intra–layer coupling and J' is inter–layer coupling.

(c) Chakravarthy–Halperin–Nelson theory :

Using the above Heisenberg Hamiltonian, Chakravarthy, Halperin and Nelson (CHN) developed a quantitative theory to account for the instantaneous spin–spin AFM in–plane correlation length as below [125].

$$\text{For } S = 1 : 1/a = \zeta_{AF} = C_1 \exp\left[2\pi\beta_s / K_B T\right], \tag{38}$$

$$\text{For } S = 1 : 1/a = \zeta_{AF} = C_2 \exp\left\{(2\pi\beta_s / K_B T)/1 + (K_B T / 2\pi\beta_s)\right\}, \tag{39}$$

where a is lattice parameter, C_1 and C_2 are constants and β_s is spin stiffness constant which is given by the expression :

$$\beta_s = JS^2 [1 + (0.158/2S)]^2 [1 - (0.552/2S)] . \quad (40)$$

At any non-zero temperature $(K_B T/J) << 1$, the AFM correlation length follows the singular form :

$$\zeta_{AF} = C_{\exp} [J/K_B T] . \quad (41)$$

The plot between $(T \ln \zeta_{AF})$ and T/J is shown in Figure 11. Thio *et al* [61] examined the role of possible Ising-like anisotropies by considering different values for coupling J_x, J_y, J_z in the Hamiltonian as below :

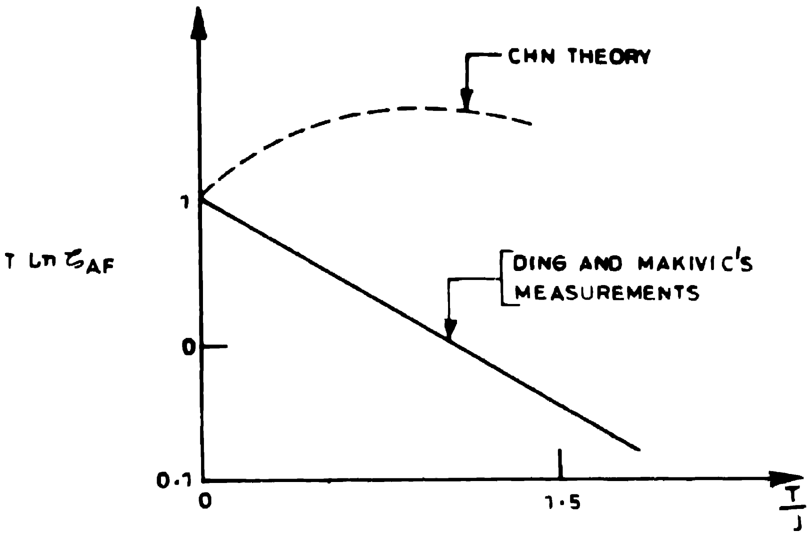

Figure 11. $T \ln \zeta_{AF}$ *versus* $\frac{T}{J}$ (adapted from [126]).

$$H = \Sigma_{ij} \left[J_x S_i^x S_j^x + J_y S_i^y S_j^y + J_z S_i^z S_j^z \right] \quad (42)$$

and found that such anisotropies have no significant role to play on spin – 1/2 system.

Mattis [127] evaluated the free energy of a single CuO_2 plane in the Ising representation for the AFM insulators La_2CuO_4 and $YBa_2Cu_3O_6$ and found that AFM is replaced by paramagnetic phase having short range order only beyond a critical concentration $x_0 = 0.29289$ holes per CuO_2 cell.

(d) Dyaloshinksy–Moriya ferromagnetic interaction :

The super-exchange intraplane interaction (leading to long-range three dimensional antiferromagnetic ordering) within the CuO_2 plane is very high with a value of $J = 0.16$ eV. However, there is a perturbation *viz.*, the antisymmetric exchange interaction of the order of 0.55 meV, which allows a weak ferromagnetic out-of-plane component of Cu^{2+} magnetic moments coupled antiferromagnetically from plane to plane along c–axis. This is the so-called Dzyaloshinsky–Moriya (DM) antisymmetric interaction. This DM interaction is due to slight rotation of the CuO_6 octahedra in the orthorhombic phase. The DM interaction is responsible for canting of the spins away from the direction of the staggered magnetization which lies in c–direction towards b–axis by a small angle.

$$\left.\begin{aligned} |D_{ij}| &\propto (\Delta g/g)J, \\ H &= 2J\Sigma_{ij}\left[S_i S_j\right] + 4\Sigma_{ij}\left[D_{ij}S_i \times S_j\right], \end{aligned}\right\} \tag{43}$$

where D_{ij} is called DM vector and Δg is the deviation in pyromagnetic ratio due to spin–orbit coupling.

Koshibae *et al* [128] found that the weak FM induced in low–temperature orthorhombic phase (LTO) of La_2CuO_4 type crystal is accompanied by a stabilisation of AFM with planar anisotropy. There are two possibilities in the low–temperature tetragonal (LTT) phase depending on the direction of the DM vector : (i) the weak FM similar to that of LTO phase and (ii) the AFM state characterised by strong uniaxial anisotropy of quantum mechanical origin. A fluctuation of chiral order state is suppressed in the former but is enhanced in the latter.

(e) Spin density waves :

Preliminary neutron work on La_2CuO_4 indicated that it may be commensurate AFM state, but the low magnetic moment equal to 0.45 μ_B determined later indicated an SDW with large amplitude. This value of magnetic moment is well below that for a local $S = 1/2$ Heisenberg condition owing to the DM interaction *i.e.*, because the p/d overlap decreases away from the d^{10} filled–shell condition. As oxygen content is changed to bring about the completion of oxygen sub–lattice, then the Cu sub–lattice will acquire vacancies. Thus, the value of T_N is determined by the perfection of Cu sublattice. Thus, the value of T_N is determined by the perfection of Cu sublattice. Because of opening of a gap near Fermi level the metallic state (predicted by band structure calculations) is driven by the SDWs into an insulating state. Thus, 2–1–4 HTSCs might be SDW superconductors. The mechanism is as follows. The end member La_2CuO_4 is a half–filled system. At high temperature, an SDW is formed because of strong correlations between d electrons. The SDW gap opens at the Fermi level and system becomes insulator. As holes are created by introducing Ba^{2+} or Sr^{2+}, the SDW will be destabilised. However, this tries to stabilise the SDW vector in the undoped system. As doping increases, this nesting feature is lost and superconductivity appears and T_c increases.

(f) Hubbard and t–J models :

The total Hamiltonian in this model consists of three terms. As has been discussed, at zero or low doping, the HTSCs have AFM insulating ground state. Thus, the starting system is Heisenberg spin–1/2 magnet characterised by the exchange integral J. To minimise the disturbance on this AFM background, the holes prefer to move in pairs forming a Bose condensate whereas the electrons can just only hop *i.e.*, move from site i to site j without any spin–flip with an amplitude determined by the transfer integral t_{ij}. The Coulomb repulsion U discourages the double occupancy of same site [129].

$$H = J \sum_{\langle ij \rangle} S_i \cdot S_j - t_{ij} \left(C_{i\sigma}^{+} C_{i\sigma} + C_{j\sigma}^{+} C_{j\sigma} \right) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} . \tag{44}$$

In this Hamiltonian, one gets the case of spin–1/2 Heisenberg if the J–term only is considered ; one gets the Hubbard Hamiltonian by considering only the t–term and U–term ; and finally, one has the case of t–J model when only the t–term and J–term are considered ; in each case, ignoring the remaining terms. If the degree of freedom of Fermi system is of itinerant type, the model is Hubbard and if it is localised type, it is Heisenberg. Typically, $U > t$ and $t = 0.5$ eV. The relation between the three characteristic energies, J, t and U is $J = (4t^2)/U$. The limit $U = 0$ represents band nature, whereas the limit $t = 0$ stands for the localisation.

(g) Magnetism in Hubbard model :

Hirsh studied Hubbard model using Monte Carlo simulation technique using the concept of spin density waves in two dimensions and predicted the following value of staggered magnetization M and gap of charged excitation Δ_{ch} [130].

$$M \propto (t/U) \exp\left[-2\pi(t/U)^{1/2}\right], \quad \text{where} \quad \Delta_{ch} = U.M. \tag{45}$$

When U is infinitely large, Hubbard model leads to Heisenberg state with $M = 0.6$ Deviations from half filling (one hole per unit cell of CuO_2 plane) lead to the appearance of a regularly spaced array of domain walls at which the holes are localized. This is called solitonic state. When the hole density equals to Δ_{ch}/t, the solitonic state smoothly transforms to a sine–wave incommensurate structure. When $U > t$, then J is positive and the electrons on nearest neighbour sites i, j get coupled antiferromagnetically and the Hamiltonian reduces to that of Heisenberg. In the limit of $U = \infty$ or $J = 0$, Nagaoka proved that the ground state for $(N-1)$ electrons on a bipartite lattice with N sites is a completely polarized ferromagnetic (FM) state. When the number of holes increases, the FM state becomes unstable because of Pauli exclusion principle. However, the limit $U = \infty$ is not physical. Inui and Doniach [131] studied a single band Hubbard model on a 2–D square lattice slightly below half–filling. Using canonical transformations and a form of variational wave function that allows an expansion in terms of hole concentration with respect to half filling, they found that a nonzero U results in a frustration of the AFM order favoured by the super exchange interaction.

(h) Mott–Hubbard insulator :

In HTSCs, $E_p = E_d$ and large band–width ≥ 9 eV. The electronic state of Mott insulator is described by Hubbard Hamiltonian and is called Hubbard band. In the absence of U, it is the half filled band. In the presence of U, it splits into two bands called Upper Habbard Band (UHB) and Lower Hubbard Band (LHB), with LHB completely filled. Because of a gap between UHB and LHB, the material acquires insulating properties.

(i) Phase diagram of Hubbard model :

Denoting the bandwidth by W, the following can be inferred from Figure 12 [132]. (i) For $U > 0$ and $W > 0$, only the two phases CDW and SDW separated by line $U = 4W$ are possible. (ii) For $U < 0$, the CDW and singlet superconducting state (SS) meet at $W = 0$. (iii) For $U < 0$ and $W < 0$, SS (on-site) pairing and d wave pairing are possible. (iv) For $U > 0$ and $W < 0$, SDW and d wave pairing are possible. Thus, the Hubbard model contains various phases such as Mott insulator, band insulator with AF ordering, conducting spiral

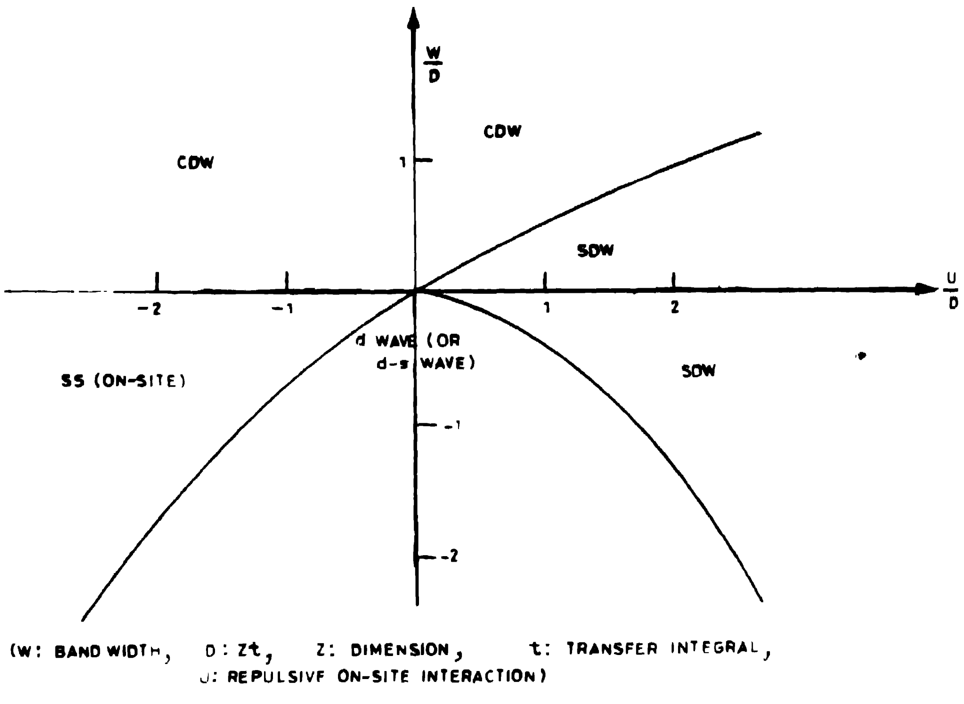

Figure 12. Phase Diagram of Hubbard Model (adapted from [132]).

spin structures, itinerant ferromagnets, Fermi liquid and a non-Fermi liquid. Kusakabe and Aoki [133] used 2–band Hubbard Hamiltonian to study the possible magnetic orders. If J and J' are exchange interactions between neighbours and next nearest neighbours respectively, stands for intra-band Coulombic repulsion ; and $J = (U-U')$ they concluded that (i) if $J < U'$, there exist AFM intra orbital correlation, (ii) if $J \approx U'$, there exist inter orbital FM correlation between nearest neighbours with staggered orbital pairing and (iii) if $J \geq U'$, there exist spin singlets between orbitals at next nearest neighbouring sites with on-site FM correlations.

(j) Fermi liquid model when $U > 4t$:

Ngyuen Manh *et al* [134] studied the case $U = W$ *i.e.*, doped AF state close to Mott transition. They concluded that the Landau paramcter is reduced with respect to that of paramagnetic Fermi liquid due to the presence of AFM fluctuations. Thus, AFM correlations are responsible for the possible singlet superconductivity in the system for $U > 4t$. This is the main difference with the conventional Fermi liquid (He–3) where triplet superconductivity is present.

(k) Anderson's RVB (spinon–holon) model :

Anderson [135] extended the spin wave theory, introduced by Holstein and Primakoff [136] for ferromagnets, to study the ground state of AF magnets with large spin S in 1952. Later in 1973, Anderson [137] stated that the ground state of two–dimensional spin–1/2 AF magnet be disordered and postulated the 'Resonance Valence Band' (RVB) state as one characterized by short-range order in which a 'spin-liquid' could be formed and this state would be a superposition of states in which the spins are locally bonded to one another. Anderson named it 'Novel quantum liquid' or 'Luttinger liquid'. At 30% doping, when an electron is removed, it leaves behind at least one spinon excitation and one holon excitation and also a smaller shower of soft collective excitations. This is supported by the angle resolved photo-emission for a sample of $Bi_2Sr_2CaCu_2O_y$ in normal state at 90 K [138,139].

(a) Spinons :

They carry spin = 1/2, charge = 0 and obey Fermi statistics. They are isolated spins floating on singlet liquid and have a longer mean free time than the transport time. They have a sharp 'pseudo' Fermi surface at K_{Fermi}, the nesting of which gives rise to antiferromagnetism.

(b) Holons :

They carry charge = e, spin = 0 and obey Bose statistics. They bose condense leading to superconductivity. However, bose condensation of mere holons gives the value of fluxoid as $\phi_0 = (hc/e)$ whereas the experimentally found value is $\phi_0 = (hc/2e)$. Hence, Wheatly and Hsu [140] proposed that pairs of holons undergo bose condensation. If b, s and e stand for singlet pair, spinon and holon respectively, then the hamiltonian is written as :

$$H_{\text{RBV}} = J \sum b_{ij}^{+} b_{ij},$$

where
$$b_{ij} = \frac{1}{\sqrt{2}} \left(s_{i\uparrow}^{+} s_{j\downarrow}^{+} - s_{i\downarrow}^{+} s_{j\uparrow}^{+} \right). \tag{46}$$

According to Anderson, the driving force for superconductivity is interlayer Josephson tunnelling. In RVB theory, the energy scale is $J = 300 - 1000$ K, rather than the BCS energy scale $W_D^0 = 100$ to 500 K. Thus, the observed high T_c values could be explained. Similarly, the exotic results of HTSCs regarding resistivity, tunnelling conductance and NMR were explained.

As regards the Hall effect, the spinons are accelerated by the magnetic field just as though they were quasiparticles [141].

$$\theta_{\text{Hall}} = \omega_{\text{cyclotron}} \; \tau_{\text{spinon}} \, . \tag{47}$$

The correlated state near the Fermi surface precesses with the unperturbed cyclotron motion.

$$\begin{aligned} 1/\tau_{\text{spinon}} &= \text{spinon–spinon scattering} + \text{magnetic scattering} \\ &= AT^2 + Bn_{mag} \, . \end{aligned} \tag{48}$$

Liu [142] defended RVB model by observing that La_2CuO_4 is an itinerant AF magnet and the fluctuating local exchange field causes the superconducting state to be gapless. But the RVB theory suffers from a drawback as follows. As pointed out above, RVB theory is a gap-less theory. But FIR reflectivity and tunnelling studies actually show the existence of a BCS energy gap as a function of temperature, with anisotropy.

(l) Laughlin's anyon model :

Anyon model was proposed by Laughlin in 1988. According to Laughlin, a magnetic flux is created by exchange interaction J of $t-J$ model. Then, Laughlin used the Holstein-Primakoff transformation for spin to show that the system of spin–1/2 on a two-dimensional triangular lattice is equivalent to a Boson system under a magnetic field with 1/2 flux quantum penetrating each unit cell in the lattice. He also asserted that there exist spinons and holons, but with different properties as below [143]. In the case of non-zero J, spinons and holons obey 1/2 statistics and are called anyons. The interchange of two anyons results in a phase-modulated wave-function as below.

$$\phi(r_1, r_2) \to \exp\left[i(p/q)\pi\right] \phi(r_1, r_2) \, , \tag{49}$$

here, P/q is a fraction. Thus, the interaction between anyons is due to the fact that each anyon carries a fraction p/q of the fluxoid. The change in phase of wave-function is determined by the flux. Two modifications were proposed as below :

(a) According to Steward [144] spinons and holons are anyonic even in the $J = 0$ limit and they acquire anyonic nature because of the transfer integral *i.e.*, the hopping matrix element t as below,

$$t \to t \, \exp\left\{ i \, (\hbar c/e) \int^{l} A \cdot dl \right\} . \tag{50}$$

The hamiltonian is :

$$H = -t \sum_{<ij>} s^{+}_{j\sigma} \, e_{j0} \, e^{+}_{i0} \, s_{i\sigma} \tag{51}$$

where, as previously in RVB model, e and s stand for holon and spinon respectively.

(b) According to Wen-Wilczakzee, the high T_c is due to spontaneous symmetry breaking.

Hetrick *et al* [145] found that for anyon superconductor, there is a new critical magnetic field H_c' such that if the external magnetic field B_{ext} exceeds H_c', a uniform magnetic field $B_{in} = (B_{ext} - H_c')$ penetrates the material (the partial meissner effect). H_c' depends on hole density (n) and effective mass (m) of carrier. However there is a temperature T_c' above which H_c' and superconducting is lost. T_c' depends on n, m^* and interplanar spacing. For anyon superconductor, the Langrangian is characterised by carrier field, electromagnetic fields and Chern–Simons gauge fields.

(m) Schriffer's spin bag model :

In the AF insulator with long-range spin order, the spin bag represents a local decrease in the spin-density-wave gap $2\Delta_{SDW}$ over a region of size which is large compared with lattice spacing 'a' in the weak coupling [3,146]. The bag causes a twist of spin quantization axis. When U is large, the spin bag corresponds to a decrease in the near-neighbour spin order around the hole. The region of decreased spin order and spin twist is co-moving with the hole and forms a 'bag' inside of which the hole lives. The combination of spin amplitude (longitudinal) and spin-twist (transverse) dynamics leads to bags and their attractive interaction between holes in the regime $U/t = 1$. Spin bags correspond to non-topological solitions. SDW amplitude is different around a carrier. On adding another carrier, it is energetically favourable for the two to be together and deform SDW amplitude locally. This is the 'spin-bag'. Since the SDW energy scale is 0.2 eV, high T_c values are possible.

(n) Self consistent renormalisation (SCR) theory of spin fluctuations :

The anomalous properties of HTSCs are explained in terms of AFM spin fluctuations on the basis of two dimensional itinerant electron model which assumes the Fermi liquid-like ground state [147]. For weak itinerant AF magnets, dynamical susceptibility around staggered component is

$$\chi_{(Q+q)}(\omega,T) = \chi_{(Q+q)}(T) \Big/ \left[1 - i\omega/\Gamma_{(Q+q)}\right] \tag{52}$$

with

$$\chi_{(Q+q)}(T) = \chi_Q(T) \Big/ \left(1 + q^2/k^2\right),$$

$$\Gamma_{(Q+q)} = \Gamma_S\left(k^2 + q^2\right),$$

$$k^2 = \chi_Q^0 \big/ A\chi_Q(T),$$

where Q is the wave vector specifying the AFM order, χ_Q^0 the susceptibility in the absence of the electron-electron interaction, the parameters Γ_S and A specify the frequency spread and the spatial correlation of the spin fluctuations, respectively.

The linear slope of the resistivity-temperature plot and the temperature of saturation value of $(1/T_1)_S$ due to the AFM spin fluctuations is determined mainly by the value of Γ_S.

(o) Hao and Clem model :

For $Hc_1 << H << Hc_2$, Ginzburg Landau equations cannot be solved in closed form. Clem [148] proposed variational model for an isolated vortex which is valid both outside and in core vicinity Hao *et al* wrote [149] interms of core radius of vortex and derived :

$$H_{c1} = \frac{k\xi_{00}^2}{8} + \frac{1}{8_k} + \frac{k_0(\xi_0)}{2kK_1(\xi_{VO})} \tag{53}$$

where ξ_{VO} is the value at $B = 0$; k is GL parameter and $K_n(x)$ is modified Bessel function of $n-th$ order.

$$H_{c2} = \frac{k}{\left(m_1 \sin^2\theta\cos^2\phi + m_2\sin^2\theta\sin^2\phi + m_3\cos^2\theta\right)^{\frac{1}{2}}} \tag{54}$$

where θ and ϕ are polar and azimuthal angles of applied field ; m_1, m_2 and m_3 are components of mass tensor.

Hao and Clem [150] derived :

$$-4\pi M = \left(\frac{\alpha\phi_0}{8\pi\lambda^2}\right) \ln\left(\frac{\beta H_{c2}}{H}\right) \tag{55}$$

where α, β are constants.

6. Other magnetic superconductors

Three compounds *viz.*, $(SN)_x$, $Ca_{0.5}Zn_{0.5}Fe_2O_4$ and La_2NiO_4 are also reported in literature as magnetic superconductors.

In 1975, Greene measured the value of T_c of $(SN)_x$ to be 0.26 K. Lou [151] reported its specific heat studies at low temperature. It follows BCS theory. The specific heat anomaly peak temperature was suppressed to 0.18 K in an applied magnetic field of 1 kG. A smeared Schottky magnetic anomaly was also induced and persisted after removal of applied field at 1 K. These results indicated the co-existence of magnetism and superconductivity in $(SN)_x$ crystals.

Kulkarni *et al* [152] carried out Mossbauer study of the compound $Ca_{0.5}Zn_{0.5}Fe_2O_4$. It consists of mixed phases, exhibits superconductivity, contains no rare earth oxides. It was prepared from CaO, ZnO and Fe_2O_3. The magnetic structure of Fe in this superconductor was probed using 14.4 keV Mossbauer resonance transition in Fe–57. They find two separate magnetic structures corresponding to the chains linked ferromagnetically and antiferromagnetically.

Guo and Temmerman [153] carried out self-consistent spin-polarised electronic band structure calculations with local spin density approximation (LSDA) for La_2NiO_4. They concluded that it exhibits semiconductivity and antiferromagnetism at low temperatures and superconductivity might occur in some doped compounds of $La_{(2-x)}M_xNiO_4$ $(0.5 < x < 1.0$

and M = Zr, Hf etc) because of the similarity in electronic band structure between La_2CuO and La_2NiO_4. This conclusion is based on the assumption that the LSDA electronic band structure is relevant to high T_c superconductivity in cuprates no matter what the pairing mechanism is. Kakol *et al* [154] reported the evidence for the co-existence of superconductivity and antiferromagnetism in pure La_2NiO_4 below the onset temperature T_{co} = 69 K. The diamagnetic moment depends on the field linearly upto the highest available field of 154 Oe. The slope varies with temperature. They observed a small remanent magnetic moment in the direction perpendicular to the NiO_2 planes.

However, there appears to be controversy about these three compounds being magnetic superconductors.

7. Conclusions

In all, 80 magnetic superconductors have been surveyed in this article. Typical results of experimental investigations like ESCA, neutron diffraction, neutron scattering, Mossbauer spectra, NMR, NQR, muon spin resonance, magnetostriction, XRD, high pressure effect and specific heat measurements on these compounds reported by various authors are outlined. As regards the theoretical explanation for them, the RE magnetic superconductors have been well understood within the frame-work of GL, BCS and AG theories while HFSCs and HTSCs are still having only approximate models without a consensus. The reason for this could be that sufficient experimental investigations on 'single crystals' are yet to be performed and the resulting data has to be carefully analysed. Only those aspects related to magnetic ordering in superconductors have been dealt with in this article.

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APPENDIX

List of the magnetic superconductors surveyed in this review

(A) *Rare–earth magnetic superconductors (RESCs)*

(*16 in number*)

$Y_{(1-x)}Gd_xOS_2$; $La_{(1-x)}Gd_x$; $Ce_{(1-x)}M_xRu_2$ where M = Ho, Tb ;

(R) Rh_4B_4 where R = Er, Nd, Sm, Tm, Lu ;

(R) Mo_6S_8 where R = Ho, Pb, Gd, Tb, Dy, Er : Y_9Co_7.

(B) *Heavy fermion magnetic superconductors (HFSCs)*

(*23 in number*)

UPt_3, URu_2Si_2, $U_{0.97}Th_{0.13}Be_{13}$, $CeCu_2Si_2$

$CePb_3$, UNi_2Al_3, $CeIn_3$, $CeRh_3B_2$, $CeSn_3$,

$Ce[Ru_{(1-x)}Rh_x]_3BN_2$, UBe_{13}, $U_{(1-x)}M_xBe_{13}$

where M = Hf, Zr, Sc, Lu, Y, Pr, Ce, Th, La ; $CeCu_2Si_2$, $CeAl_2$, $CeAl_3$

(C) *High T_c magnetic superconductors (HTSCs)*

(*38 in number*)

$[La, Sr / Ba / Ca]_2CuO_4$, La–(Ba, Nd / Sm) –Cu–O, Y–Ba–Cu–O,

(RE) –Ba–Cu–O where RE = Sm, Eu, Gd, Dy, Ho, Er, Tm, Nd ;

Y–Ba–[Cu–Fe]–O, Gd_2CuO_4, $GdCo_xBa_2Cu_3O_7$, $Gd_{1.85}Sr_{0.15}CuO_4$,

[Y–Fe]–Ba–Cu–O, $EuBa_2[Cu_{(1-x)}Zn_x]_3O_{(7-y)}$, Pr–Ba–Cu–O,

R–Ba–K–[Cu–Fe]–O where R = Y, Pr ; [Y–Dy]–Ba–[Cu–Ni]–O,

Ca–La–Ba–[Cu–Fe]–O Tl–Ba–Y–Cu–O, Nd–Ce–Cu–O, Y–Sr–Cu–O,

Ln–Cu–O where Ln = Nd, Sm, Pr ; Sm–Ba–Cu–O, Bi–Sr–Y–Cu–O,

Bi–Sr–[Y–Ca]–O, Bi–[Sr–Ca]–Mn–O, Bi–Sr–Co–O, Eu–Ba–[Cu–Zn]–O,

Pr–[Ba–Pr]–Cu–O, Pr–Gd–Ba–Cu–O

(D) *Other magnetic superconductors*

(*3 in numbers*)

$(SN)_x$, Ca–Zn–Fe–O and La_2NiO_4

Total number of magnetic superconductors surveyed : 80

About the Reviewers

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