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Nuclear magnetic resonance and bulk magnetism

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Abstract : The paper reviews the power of nuclear magnetic resonance (NMR) technique by giving few examples of studies in solids and their correlation with bulk magnetism. As illustration, the investigation in some transition metal and rare earth alloys are discussed NMR shift of specific nuclei from that of a diamagnetic solid are correlated to the nature of magnetism in the solids In the ordered or paramagnetic state, the local field at the nucleus is proportional to the magnetic moment of the magnetic ion either directly or through the polarization of the conduction electrons at different nuclear sites Examples in spin glass, and superconductors are presented

Keywords NMR, magnetic materials, bulk magnetism

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1. Introduction

The magnetic resonance frequency ω_0 of a nucleus is directly proportional to the externally applied magnetic field H_0 and γ, the gyro magnetic ratio of the nucleus ($\gamma = \mu / I\hbar$). In addition to H_0, local fields H_{loc} will alter the resonance frequency ω_0 to ω.

$$\omega = \gamma(H_0 + H_{loc}). \qquad (1)$$

The local fields can be due to several reasons, *viz.* chemical, conduction electron hyperfine interaction I.S. (I = nuclear spin, S = ionic spin state), and internal magnetic fields which may be static or time varying and may add or subtract to the external magnetic field. In the paramagnetic systems, H_{loc} is proportional to the magnetism and susceptibility χ of the ion and in the magnetically ordered systems to ordered magnetic moment of the magnetic ions, suitably modified at different nuclear sites. In this sense, bulk magnetism through susceptibility or magnetization and NMR are related to each other ; with the former as macroscopic probe and the latter as microscopic probe. Since Professor K. S. Krishnan was greatly involved in the magnetism and the magneto chemistry of materials, this article is dedicated to him during his birth centenary years. The author had also the privilege of personally discussing with Prof. K. S. Krishnan the techniques like NMR, Mössbauer effect and the neutron scattering with special reference to the magnetism of materials.

2. Transition metal alloys

Platinum in a transition metal with an atomic configuration $5d^9 6s$ and has Pt^{195} isotope with spin $I = 1/2$. The temperature dependent paramagnetism comes from the unfilled *d* band. ($\chi = 1 \times 10^{-6}$) emu/gm at 300 K,. 1.10×10^{-6} emu/gm at 80K) (1). The Knight Shift (KS), which is the NMR frequency shift of Pt^{195} in metal from that of a reference compound is –3% at 300K and –3.5% at 80K, arises from the core polarization of *s* electrons due to unfilled *d* electron spins and normal I.S interaction from conduction electrons. The paramagnetism arising from *d* band can be modified by suitable alloying with metals like tin, lead or mercury [1]. The large negative Knight Shift gets reduced considerably on alloying with weak or no temperature dependence and even becomes positive due to the absence of *d* electrons. The susceptibility of the alloy then behaves like a pauli paramagnet [1]. The Knight shift data is illustrated in Table 1 in the temperature range of 110 K to 300K (1).

Table 1. Knight shift in platinum alloys.

Alloy	Pt%	K.S. at 300K	K.S. at 110K
Pt metal	100	–3%	–3 5%
Pt_3Sn	75	–0.32%	–0.44%
PtSn	50	+0.37%	+0.37%
Pt_3Pb	75	–0.29%	–0.46%
$PtHg_2$	33	+0.3%	+0.3%

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3. NMR in ferromagnets

The observation of NMR in ferromagnetic cobalt metal was first made by Gossard and Portis [2] without any external field (zero field NMR) at a high frequency of 213.1 MHz, corresponding to an internal field of 21.3 tesla at Co^{59} nucleus at 300K, which is largely temperature dependent. Soon the resonance of the Fe^{57} and Ni^{61} was observed without external fields in ferromagnetic iron and nickel corresponding negative internal fields of 33 tesla and 10 tesla respectively. The resonance fields follow the bulk magnetization and are related to the moment of the magnetic ions in these cases.

4. NMR in rare earth alloys

The problem of the polarization of the conduction electrons in a metal by a localized spin is very crucial to the understanding of ferromagnetism in $3d$ and $4f$ metals. The essential point is that the d or f spins impressed a uniform or oscillatory polarization upon the conduction electrons, which then couple the rare earth or transition metal ions to order magnetically. NMR can probe this at the nuclear site through zero field NMR technique at nuclear sites of magnetic ion or at the alloying site due to resonance shift which can be correlated to the bulk susceptibility. (K_d or K_f α χ_d of χ_f). Two examples are given below : (a) Rare earth Pt_2 (RPt_2) and (b) Rare earth Pt_5 (RPt_5) alloys where Pt atoms are in two inequivalent crystallographic sites.

The RPt_2 compounds have cubic Laves structure ($MgCu_2$) with all the platinum atoms equivalent. The alloys $LaPt_2$, $CePt_2$, $PrPt_2$ and $NdPt_2$ have increasing rare earth magnetic moment. $LaPt_2$, with no f electron, is a reference compound [3].

(i) $LaPt_2$: K = 0.75% at all temperatures,

(ii) $CePt_2$: $\chi = 3 \times 10^{-3}$ emu/mole K = + 1% at 400K
$\chi = 5 \times 10^{-3}$ emu/mole K = + 1.4% at 80K,

(iii) $PrPt_2$: $\chi = 6 \times 10^{-3}$ emu/mole K = 2.2% at 400K
$\chi = 10 \times 10^{-3}$ emu/mole K = + 2.8% at 80K,

(iv) $NdPt_2$ $\chi = 8 \times 10^{-3}$ emu/mole K = + 2.9% at 400K
$\chi = 12 \times 10^{-3}$ emu/mole K = + 4.2% at 80K.

(χ is mostly influenced by 4f electrons)

The RPt_5 compounds ($CaCu_5$ structure), Pt atoms exist in two inequivalent sites Pt_I and Pt_{II} in 2:3 ratio and the polarization at the two sites is found to be oscillatory, not uniform because two distinct resonances are observed with different temperature dependent slopes [3].

(i) $LaPt_5$: Pt_I K% = 0.1% Pt_{II} = +1% at 400K (Reference compound),

(ii) $CePt_5$: Pt_I K% = + 0.3% Pt_{II} = + 1.2% at 400K
+ 0.4% + 1.6% at 80K,

(iii) $PrPt_5$: Pt_I K% = + 0.7% Pt_{II} = +1.3% at 400K
+ 1.3% +1.5% at 80K

(iv) $NdPt_5$: Pt_I K% = + 1.2% Pt_{II} = + 1.8% at 400K
+ 1.8% + 2.3% at 80K

5. NMR and "Antiferromagnetic" Cu_2Sb alloy

Cu_2Sb has two inequivalent copper sites with Cu_I and Cu_{II} having tetragonal site symmetry. One observes quadrupolar split NMR lines from the two sites from 420K to 77K without any appreciable change in the Knight Shift and linewidth. However this alloy is from magnetic susceptibility and specific heat measurement reported as an antiferromagnet with $T_N = 373K$ with μ_{eff} as 2.6 Bohr magnetron [4]. However, NMR shifts are small, about 0.1%. It is clear that if antiferromagnetism comes from copper ions, the NMR lines would have drastically changed on passing through the magnetically ordering temperature. So it is clear that Cu_2Sb is not an antiferromagnet but a simple Pauli paramagnet. This example shows the power of a microscopic probe like NMR over bulk probes like magnetization, specific heat etc.

6. Spin glass Co-Ga systems

Cobalt Gallium alloys (Co_xGa_{1-x}, $x = 0.35 \le x \le 0.75$) have CsCl structure. In a well-ordered equiatomic alloy ($x = 0.50$), cobalt has no magnetic moment and can be regarded as a nonmagnetic matrix. For $x > 0.50$, the excess Co atoms go to Ga site, giving rise to spin glass like magnetic properties. Basically excess cobalt goes to gallium (antistructure) site surrounded by eight cobalt atoms, forming a magnetic cluster in a nonmagnetic matrix. One can observe spin glass features in a.c susceptibility up to $x = 0.63$ ($x > 0.63$ becomes ferromagnet). NMR of Co^{59} (zero field configuration) from cluster cobalt atoms and normal field NMR from the rest of the nonmagnetic CoGa system can be seen modified by the presence of Co clusters with differing sizes and differing spin freezing temperature [5].

In the paramagnetic state, Knight Shift Co^{59} and $Ga^{69,71}$ are 0.25% and 0.05%, independent of temperature and x. It presumably comes from the general CoGa system, unaffected by antistructure cobalt atoms. In addition a satellite Co^{59} was observed for $0.50 \le x \le 0.56$ with Knight Shift changing from − 1.5% to −2.5% in a temperature range of 400 to 200K, with large changes in the linewidth. This shows the power of NMR to "see" both magnetic and nonmagnetic atoms at the same time. On going to liquid helium temperature, the spins of these antistructure cobalt atoms freeze to give zero field NMR lines with differing local internal fields from 4 tesla onwards from "magnetic" cobalt in these cluster spin glass system, while NMR from "normal" cobalt from Co-Ga matrix can also be simultaneously observed using external field [5].

7. Borocarbide superconductors

The discovery of superconductivity in quaternary rare earth transition metal borocarbide ($RENi_2B_2C$) raises some important questions regarding superconductivity and magnetism [6]. The transition metal like Nickel and rare earth atoms like, Dy, Ho, Er, Tm have large magnetic moments. Still in $RENi_2B_2C$, superconductivity is seen at fairly high temperatures, while magnetic ordering due to rare earth moments also takes place [6].

$DyNi_2B_2C$	$T_{s.c} = 6K$	$T_{neel} = 11K$,
$HoNi_2B_2C$	$T_{s.c} = 8.5K$	$T_N = 8K$,
$ErNi_2B_2C$	$T_{s.c} = 11K$	$T_N = 6.5K$,
$TmNi_2B_2C$	$T_{s.c} = 11K$	$T_N = 1.5K$,
YNi_2B_2C	$T_{s.c} = 15.5K$	

As an example, the NMR of B^{11} nucleus in YNi_2B_2C where there is no *f* electrons but only *d* electrons from Nickel atoms is briefly presented here. It has $ThCr_2Si_2$ structure and boron atoms have uniaxial symmetry. NMR of B^{11} shows quadrupolar broadened line ($I = 3/2$) with $\nu_Q = 0.7$ MHz and a small Knight shift of + 0.06% which decreases to + 0.05% in the superconducting state [7]. Though crystallographically, all boron atoms are equivalent, two NMR lines are seen, with one of them moving to higher fields as temperature is lowered through T_{sc} and the other signal is nearly constant with the change of temperatures. It is speculated that the former belongs to the regions of the superconducting state, while due to chemical disorder between carbon and boron atoms, the latter stays in normal region. From the relaxation time studies, it is inferred that nickel atoms may carry magnetic moments. YNi_2B_2C may be considered as itinerant antiferromagnetic spin fluctuating material where electronic correlations play an important role [7]. NMR of boron nucleus in other borocarbides will be very interesting in view of the coexistence of magnetism and superconductivity.

8. Conclusion

The technique of NMR in understanding bulk magnetism is shown with examples from transition metal and rare earth alloys. Due to the brief nature of this article, NMR of rare earth nuclei in rare earth alloys and transition metal based Heusler alloys are not mentioned. The example of spin glass shows how NMR can be used to probe microscopically the presence of magnetic and non magnetic regions. In some cases, this technique is unique in deciding the magnetic nature of the material. NMR can throw a lot of insight in understanding the nature of cooperative phenomena like magnetism and superconductivity.

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