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Study of electronic structure, insulator metal transition and superconductivity in high *Tc* and related systems

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Abstract : In this review, we report band structure calculations of the layered perovskites of the type A_2BO_4 (B = Cu, Ni) and cubic perovskites of the type ABO_3 (A = La/Sr ; B = Ti, Ni, Cr, Fe and Co). The band structure and superconductivity observed in the intermetallics $BaRh_2$ and $LaRu_2$ are also reported. High pressure band structure calculations on $BaPbO_3$ as well as on some elemental solid systems were performed to throw light on insulator-metal transitions. A correlation between electronegativity and superconductivity was established. This led to the formulation of one of the criteria for an oxide compound to become a superconductor. This also gave an alternate method to find the pressure required to drive an elemental metal to become a superconductor. Our band structure studies made us to conclude that the $s \to d$ electron transfer mechanism which has been accepted in elemental solids should hold good for compounds as well. The band structure results obtained, especially for ABO_3 type compounds, are compared with the qualitative observations that have been made by Goodenough. The importance of including magnetic correlations as well as the effect of the high degree of directionality in the bonding in high T_c oxides are highlighted. Microwave absorption studies were also carried out on high T_c oxides which were prepared with different substitutions.

Keywords : Superconductivity, electronic structure, energy bands, high pressure, intermetallics, microwave absorption.

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Plan of the Article

1. Introduction

From the theoretical standpoint, the phenomenon of superconductivity in the conventional superconductors has been well-explained from Bardeen-Cooper-Schrieffer (BCS) theory. As far as their superconducting transition temperature (T_c) was concerned they were calculated from their electronic structure outputs in conjunction with McMillan's (1968) formula. There are number of elements in the periodic table which become superconductors when subjected to high pressures and this phenomenon too has been well explained using the conventional BCS theory (Asokamani 1986, Asokamani *et al* 1987, 1989).

Apart from the widely prevalent view that BCS mechanism will not work for the newly found high T_c superconductors, there are problems even with respect to their electronic structure calculations. This is an unsolved problem for the past few decades starting from the case of NiO. The conventional band theory within the local density approximation (LDA) has not been able to give the correct antiferromagnetic (AFM) ground state solution for Mott-insulators. However, it should be noted that the excited state properties of the AFM oxide compounds could be understood still with the help of band structure results. In this connection it is noteworthy to point out the observation made by Pickett (1989) that the theoretical density of states obtained from band structure calculation for all oxide superconductors exhibit good overall agreement with the experimental photoemission studies. With this in view, the band structure calculation of the layered perovskites La_2CuO_4 and La_2NiO_4 were performed. All the band structure calculations described here have been performed by using self-consistent Linear Muffin-Tin Orbital (LMTO) method (Andersen 1975, Skriver 1984).

2. The LMTO method

The energy band problem may be separated into two parts, one which depends on the one electron potential and the atomic volume, and the other on the crystal symmetry. To solve the one-electron problem in the solid, one has to construct a crystal potential. Let us consider a crystal with one atom per primitive cell. Consider a sphere of radius S_{MT} centred at the atom. Within the sphere the potential $V(r)$ is assumed to be spherically symmetric and it is assumed to have a value V_{MTZ} outside the sphere, i.e., in the interstitial region between the spheres. V_{MTZ} is known as the muffin-tin zero. This kind of potential is designed to facilitate the matching of wave functions from cell to cell through the assumption that the electrons propagate freely between the spheres with a constant wave number $k = \sqrt{E - V_{MTZ}}$. The justification behind this is that the wave length $\frac{2\pi}{k}$ is large when compared with the thickness of the interstitial region. Thus we define the potential as

$$V_{MT}(r) = \begin{cases} V(r) - V_{MTZ} & r \leq S_{MT} \\ 0 & r \geq S_{MT} \end{cases} \tag{1}$$

We now seek the solution of the Schrödinger equation

$$[-\nabla^2 + V_{MT}(r) - k^2]\,\Psi_L(E, r) = 0 \tag{2}$$

for all values of k^2, for an electron moving in the potential from an isolated muffin tin well embedded in the flat potential V_{MTZ}. In this case, the spherical symmetry spreads throughout and the wave functions are

$$\Psi_L(E, r) = i^l Y_l^m(r)\,\Psi_l(E, r) \tag{3}$$

Where L denotes the quantum numbers l and m, i^l is a phase factor and $Y_l^m(r)$ is a spherical harmonic. Inside the MT sphere the radial part $\Psi_l(E, r)$ has to be regular at the origin in order to be normalisable. It is obtained by numerical integration of the radial Schrödinger equation

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{MT}(r) - k^2\right] r\,\psi_l(E, r) = 0 \tag{4}$$

In the region of constant potential the solutions of (2) are spherical waves with wave number k and they satisfy (4) with $V_{MT}(r) = 0$:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - k^2\right] r\,y_l(k, r) = 0 \tag{5}$$

This is the well known Helmholtz wave equation. We may take the two linearly independent solutions to be the spherical Bessel function $j_l(kr)$ and the Neumann function $n_l(kr)$. In the small kr limits.

$$\left.\begin{aligned} j_l(kr) &\rightarrow \frac{(kr)^l}{(2l+1)!!} \\ n_l(kr) &\rightarrow -\frac{(2l-1)!!}{(kr)^{l+1}} \end{aligned}\right\} \quad kr \Rightarrow 0 \tag{6}$$

where the double factorial is defined by !! = 1.3.5......and – 1 !! = 1. The asymptotic forms are

$$
\left.\begin{array}{l}
j_l(kr) \rightarrow \dfrac{\sin\left(kr - \dfrac{l\pi}{2}\right)}{kr} \\[2ex]
j_l(kr) \rightarrow \dfrac{\cos\left(kr - \dfrac{l\pi}{2}\right)}{kr}
\end{array}\right. \qquad kr \Rightarrow \infty \tag{7}
$$

Thus only $j_l(kr)$ is regular at the origin while both are regular at infinity.

The LMTO method is elegant as the muffin tin orbitals (MTO) constitute a popular and efficient basis set for first principles electronic structure calculations in solids. Its advantages are the following : (1) It is applicable to materials composed of atoms from any part of the periodic Table. (2) It is minimal in the sense that per site only one *s*-orbital, three *p*-orbitals, five *d*-orbitals and seven *f*-orbitals are needed. (3) The linear MTOs which constitute an energy independent set are correct to first order in energy. (4) The set is complete for the MT potential used for its generation but is not restricted to treating MT potentials alone. (5) The MTOs may be expanded about other sites in terms of numerically evaluated radial functions, spherical harmonics and canonical structure constants. This together with the atomic sphere approximation (ASA), according to which the MT spheres are replaced by overlapping (space filling) Wigner Seitz (WS) spheres, leads to a factorization of the matrix elements into a product of structure constants and radial integrals. (6) Also, the MTOs are automatically orthogonal to the core states.

To obtain the MTO we start with the wavefunction,

$$
\Psi_L(E, k, r) = i^l Y_l^m(r) \begin{cases} \Psi_l(E, r) + k \cot(\eta_l)\, j_l(kr) & r \le S_{\mathrm{MT}} \\ k n_l(kr) & r \ge S_{\mathrm{MT}} \end{cases} \tag{8}
$$

where cot (η_l) is the constant of integration. Cot (η_l) is the equivalent of the potential function defined below. It can be obtained by applying the boundary condition that the function should be continuous and differentiable at the sphere boundary $r = S_{MT}$.

The MTOs are made energy independent and the use of the variational principle has the advantages that it leads to an eigen value problem and that it is possible to include non-MT perturbations to the potential. The LMTO secular matrix may now be written in the form H-EO which corresponds to the generalised eigen value problem.

$$
\sum (H_{LL'} - E^j O_{LL'})\, a_L^{jk} = 0 \tag{9}
$$

where $H_{LL'}$ is the Hamiltonian matrix element and $O_{LL'}$ is the overlap matrix element, may be solved by efficient numerical techniques to give the eigen values E^{jk} and eigen vectors a^{jk}

2.1. *Many atoms per cell :*

It is indeed possible to apply the LMTO formalism to molecules and compounds. In a crystalline solid let us consider a primitive cell with h atmos centred at positions q. Some of these atoms may be of the same type and we denote the number of type t atoms in the cell by h_t. In the ASA, each atom is surrounded by a sphere of suitably chosen radius S_t subject to the constraint

$$\sum \frac{4}{3} S^3 h_t \quad \Omega \tag{10}$$

$$\sum h_t = h \tag{11}$$

where by the collection of h spheres has the volume Ω of the primitive cell. Also we define an average atomic sphere S by

$$\frac{4}{3} S^3 h = \Omega \tag{12}$$

which is used to calculate the canonical structure constants.

An important new contribution to the potential comes through the Madelung term which arises due to the fact that the atomic spheres need no longer be neutral. Keeping these additional definitions in mind, the LMTO formalism is suitably modified to obtain a general procedure to calculate the energy eigen values for molecules and compounds.

2.2. *Calculation of the electron phonon coupling constant and superconducting transition temperature (T_c) :*

Estimates of the electron-phonon coupling constant λ and superconducting transition temperature may be made using our band structure results, the rigid atomic sphere approximation and the strong coupling theory. The McMillan's (1968) equation for strong coupled system expresses the T_c as,

$$T_c = \frac{\theta_D}{1.45} \exp\left[\frac{-1.04\,(1+\lambda)}{\lambda - \mu^*\,(1+0.62\,\lambda)} \right] \tag{13}$$

where θ_D is the Debye temperature and the electron-phonon coupling constant λ is defined as,

$$\lambda = \frac{\eta}{M <w^2>} \tag{14}$$

where the Hopfield parameter

$$\eta = N(E_F) <I^2> \tag{15}$$

Here M is the atomic mass and $<\omega^2>$ is the average of the square of the phonon frequency, approximated by $<\omega^2> = 0.5\theta_D^2$. We have widely used the Gaspari-Gyorffy (GG) (1972) formula to calculate η in our earlier calculations where we had used Muffin-Tin spheres. As we use the atomic sphere approximation (ASA) here, we calculate the matrix element

$M_{l,l+1}$ following Skriver and Mertig (1985). The matrix element is expressed in terms of logarithmic derivatives instead of the usual phase shifts that are used in the GG formula. The matrix element is given as,

$$M_{l,l+1} = -\emptyset_l\emptyset_{l+1} \left\{(D_l - 1)(D_{l+1} + 1 + 2) + (E_F - V(S) S^2)\right\} \tag{16}$$

D_l and D_{l+1} are the logarithmic derivatives of the wavefunctions $\emptyset_l$ and $\emptyset_{l+1}$. All these quantities are evaluated at the sphere radius S and at the Fermi energy E_F. $V(S)$ is the potential at the sphere radius and $<I^2>$ is the average of the square of the matrix elements $M_{l,l+1}$.

The electron electron interaction parameter μ^* was calculated using the Bennemann and Garland (1971) formula,

$$\mu^* = \frac{0.26\,N(E_F)}{1 + N(E_F)} \tag{17}$$

where $N(E_F)$ is the total density of states at E_F expressed in state/eV/atom.

For the case of compounds, λ in (14) is split up as (Gomersall and Gyorffy 1974, Klein Papaconstantopoulos 1976 and Huang *et al* 1988),

$$\lambda = \sum_a \frac{\eta_a}{M_a <\omega^2>} \tag{18}$$

where *a* refers to the different atomic species.

The work of the following sections is based on the theory elucidated in this section.

3. Band structure of inorganic compounds and elements

According to Goodenough's (1971) chemical arguments in the cubic perovskites of ABO_3 structure, only B-O interaction is important. In the layered perovskite structures A_2BO_4 also it was found that the interaction which is of primary importance is the B-O interaction. It is interesting to observe from the classification made by Goodenough (1971) that most of the ABO_3 compounds are metallic while some of them are AFM depending upon the *S* value of the *B*-cation. Some in the A_2BO_4 crystal structure are AFM insulators whereas others are non-magnetic (NM) insulators. Therefore in solids of ABO_3 crystal structure we come across AFM insulators. NM insulators, metals which are either Pauli paramagnetic or of Curie-Weiss kind. However, it is important to note the analogy between the phase diagrams of A_2BO_4 (which has mostly 2-dimensional character), one dimensional organic polymers and the *T-b* diagram of Goodenough (1971). These observations made us to concentrate on oxides, sulphides and tellurides and all materials which are at the verge of insulator-metal transition. It is inferred that those materials which are at the verge of *I-M* transition are the candidates which will become superconductors either under doping (chemical pressure) or under external pressure. With this as the motivation, we investigated a number of compounds of ABO_3 type such as $LaNiO_3$, $LaTiO_3$, $SrCrO_3$, $SrFeO_3$, $SrCoO_3$, intermetallics with $MgCu_2$ crystal structure, monosulphides of Fe, Co, Ni etc., some of the disulphides and also the band structures of some of the elements under high pressure. Some of the solids which were studied are at the border of *I-M* transition (Wilson 1985). Further we studied the band structure of $BaPbO_3$ under high pressure.

3.1. *Electronic structure of A_2BO_4 (A = La ; B = Cu, Ni) compounds :*

3.1.1. *Electronic structure of La_2CuO_4 :*

Since the discovery of superconductivity above 30K in La-Sr-Cu-O system by Bednorz and Muller (1986), other systems having Higher T_cs have been found. As a first step towards the understanding of their electronic properties, the band structure calculation of La_2CuO_4

Table 1. Lattice constants and sphere radii of bct La_2CuO_4 (in a.u).

a	7.146
c	25.036
S_{La}	3.650
S_{Cu}	2.688
S_{01}	2.101
S_{02}	2.101

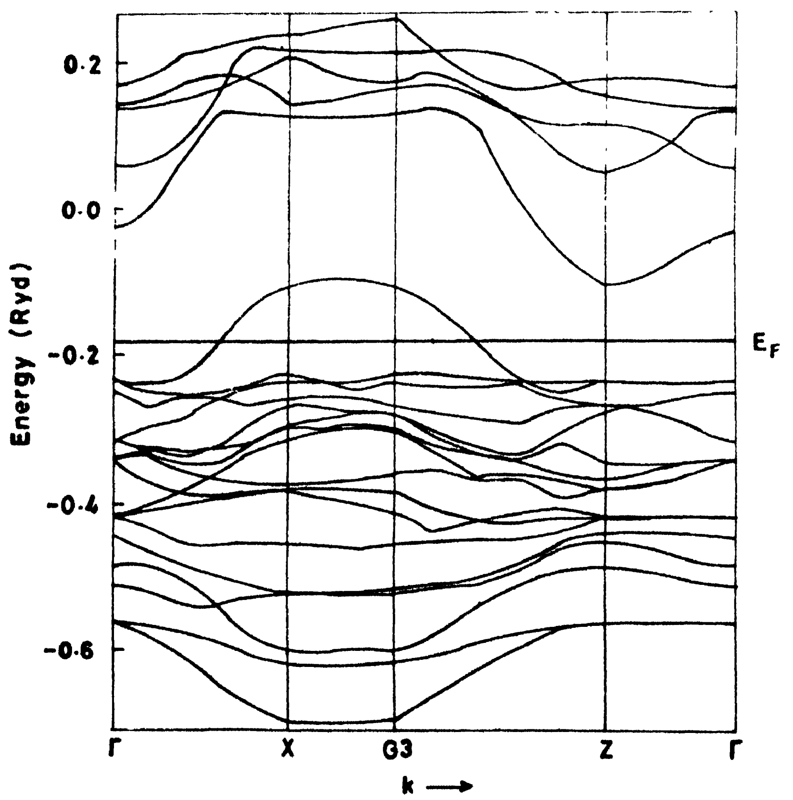

Figure 1. Band structure of La_2CuO_4.

was carried out (Subramoniam *et al* 1989b). The lattice constants corresponding to the body centered tetragonal (bct) phase of La_2CuO_4 and the sphere radii of the atoms are given in Table 1. The sphere radii were chosen such that the potential continuity is maintained at the points where the muffin-tin spheres touch each other. Barth-Hedin exchange correlation scheme was used in the construction of the potential. The band structure calculation was performed for 140 *k*-points in the irreducible wedge of the Brillouin zone and the eigen values were calculated to an accuracy of 1mRyd. The calculated band structures and the density of states histograms are shown in Figures 1 and 2.

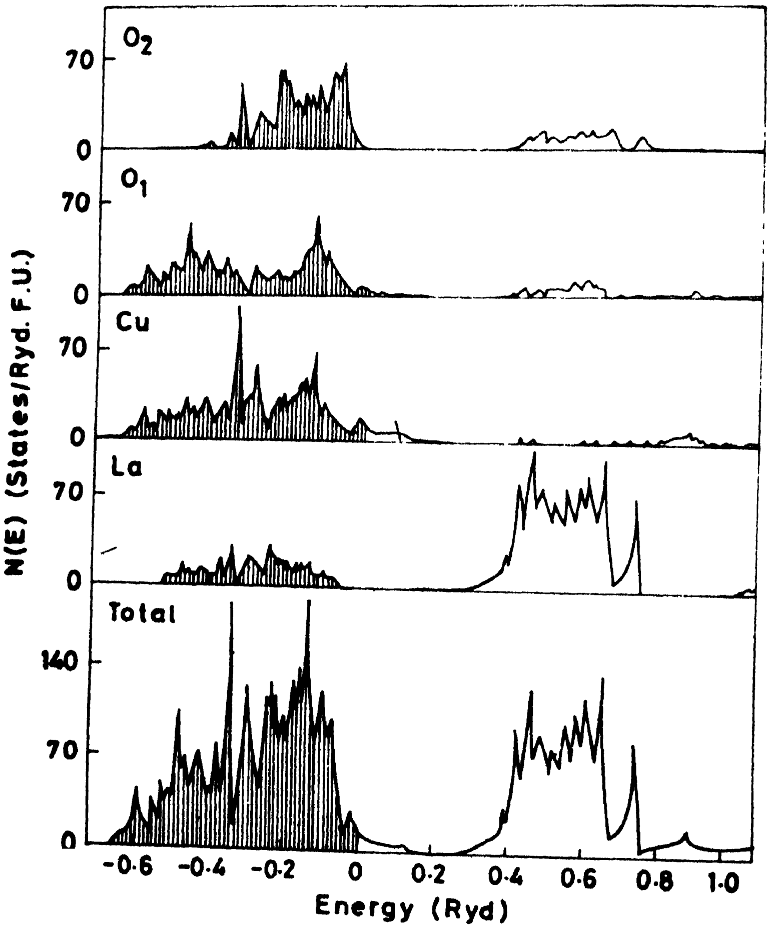

Figure 2. Density of states and their partial contribution of La_2CuO_4.

The bands obtained were very similar to those that have been determined by earlier workers (Fujiwara and Hatsugai 1987, Mattheiss 1987, Oguchi 1987, Pickett *et al* 1987 and Takegahara *et al* 1987). The density of states as well as their partial contributions at the Fermi energy are given in Table 2 and compared with other reported works. The bands that cross the E_F mainly arise from Cu-3*d* and O-2*p* orbitals.

Table 2. Comparison of the density of states at E_F of the present work with the earlier works.

	$N(E_F)$ States/Ryd. formula Unit	Partial density of states (States/Ryd.-Formula Unit)				Method	Conduction Band width	γ
		La	Cu	Oxl	Ox2		(Ryd.)	(mJ/mol K^2)
Present work	21.474	0.415	12.006	3.215	1.346	LMTO	0.520	3.54
Takegahara	26.33	—	—	—	—	APW	—	4.50
Fujiwara	22.50	0.350	13.120	3.170	1.160	LMTO	—	—
Mattheiss	17.952	—	—	—	—	LAPW	—	—
Pickett	16.871	—	—	—	—	LAPW	—	—

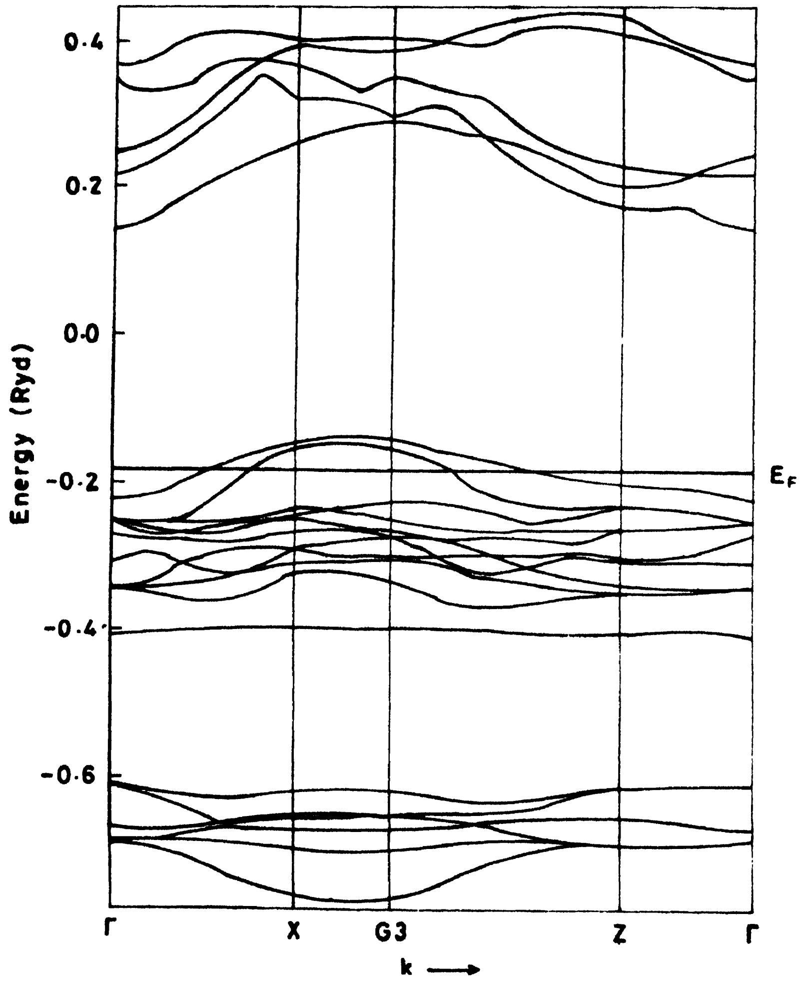

Figure 3. Band structure of La_2NiO_4.

3.1.2. Electronic structure of La_2NiO_4 :

The paramagnetic band structure of La_2NiO_4 which is iso-structural with La_2CuO_4 was determined (Subramoniam *et al* 1989a). The bands which cross the are due to Ni and O atoms. The band structure was compared with the only available calculation which is due to that of Guo and Temmerman (GT) (1988). The gross features are similar. The band structure and the density of states are given in Figures 3 and 4. The value of $N(E_F)$ is 26 states/Ryd-F.U. whereas GT get a value of 34 states/Ryd.-F.U.

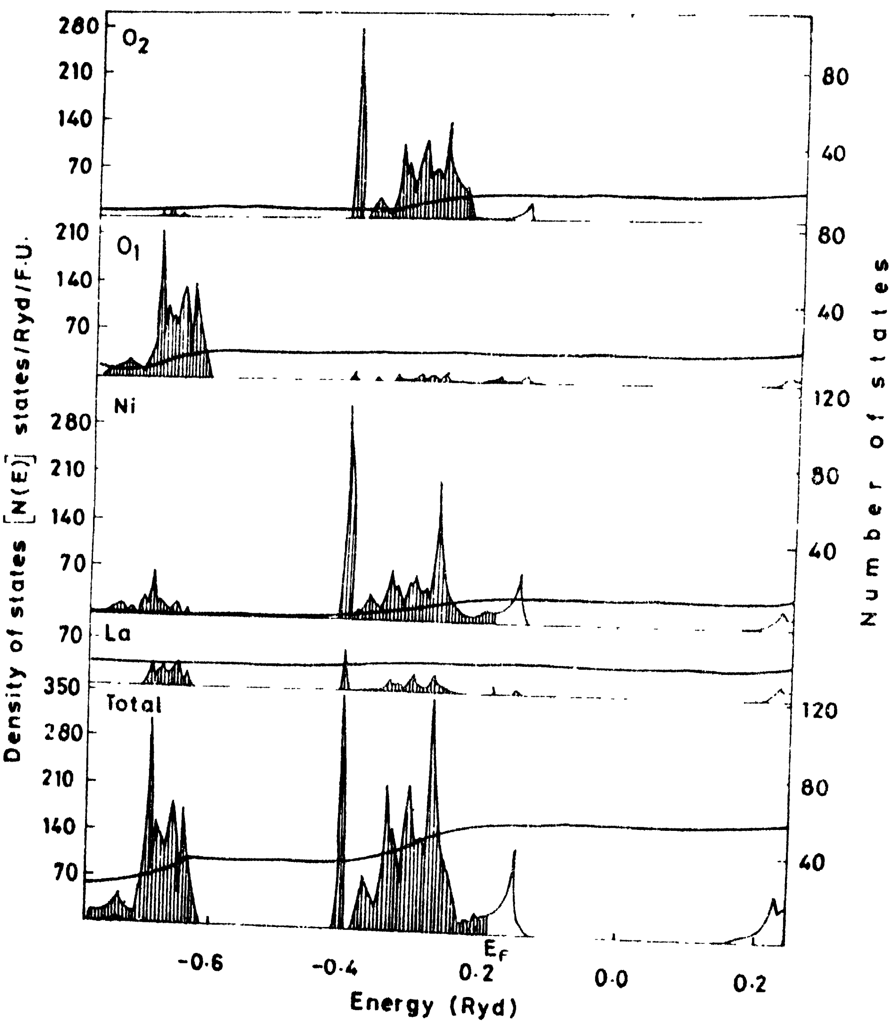

Figure 4. Density of states and their partial contribution of La_2NiO_4.

The ferro and antiferromagnetic calculations performed by GT show that antiferromagnetism collapses if the number of k-points considered in the IBZ is less than 105. We could observe this in our calculation on AFM Cr.

3.2. *Electronic structure of ABO_3 compounds :*

3.2.1. *Electronic structure of $LaNiO_3$ and $LaTiO_3$:*

The first electronic structure calculations of $LaNiO_3$ and $LaTiO_3$ performed are reported (Mathi Jaya *et al* 1989a-1989d). These cubic perovskites are Pauli paramagnetic metals. The empirical band scheme of Goodenough (1971) states that the density of state (DOS) at Fermi level is due to the B-O overlap whereas the present band structure results show a finite contribution of DOS at Fermi level from *A*-cation also. Contrary to Goodenough's statement we observe a substantial contribution to $N(E_F)$ coming from *A*-cation also.

The electronic specific heat coefficient calculated in the $LaNiO_3$ is compared with the experimental value are given in Table 3. The calculated conduction band widths are found to be 0.292 and 0.296 Ryd respectively for $LaTiO_3$ and $LaNiO_3$. The Pauli paramagnetic susceptibility values are also given in Table 3. Our experience with regard to band structure calculations of A_2BO_4 and ABO_3 compounds showed that the selection of sphere radii is far more easier in ABO_3 compounds than A_2BO_4 compounds. The reason being that in the former case there is cubic symmetry whereas in the latter, $Cu\text{-}O_6$ octahedron is elongated along the c-axis.

3.2.2. *High pressure electronic structure of $BaPbO_3$:*

The band structure calculation of $BaPbO_3$ was performed for $\frac{V}{V_0} = 1.1, 1.0, 0.9$ and 0.8. It is well known that $BaPbO_3$ becomes superconducting with Bi doping ($BaPb_{1-x}Bi_xO_3$) has a T_c of 13K at $x = 0.3$. Since the radius of Bi atom is larger than Pb atom, we felt that with substitution of Bi the cell volume will contract similar to the application of external pressure. The band structure calculations were performed for arbitrary cell volumes and the corresponding superconducting transition temperatures were calculated using the McMillan's formula (13).

Table 3. The values of γ and χ_{Pauli} along with the experimental susceptibility value.

	γ MJ/Mole-k^2	$\chi_{bs}10^{-4}$ emu/mole	$\chi_{expt}10^{-4}$ emu/mole
$LaTiO_3$	5.781	0.791	—
$LaNiO_3$	10.469	1.433	8.695

The band structures corresponding to normal pressure and for $\frac{V}{V_0} = 0.9$ are given in Figures 5 and 6. The value of electron-phonon coupling constant λ was found to increase with pressure. The parameters related to the calculation of T_c are given in Table 4. However,

Table 4. E_F, $N(E_F)$, μ^*, η, λ and T_c of $BaPbO_3$ at $\frac{V}{V_0} = 0.9$.

$\frac{V}{V_0}$	E_F Ryd.	$N(E_F)$ states/Ryd. atom/spin			μ^*	η $\left(\frac{eV}{Å^2}\right)$			λ			T_c (K)
		Ba	Pb	O		Ba	Pb	O	Ba	Pb	O	
0.9	0.425	3.663	0.936	0.900	0.134	0.410	0.108	3.560	0.093	0.016	0.535	3.090

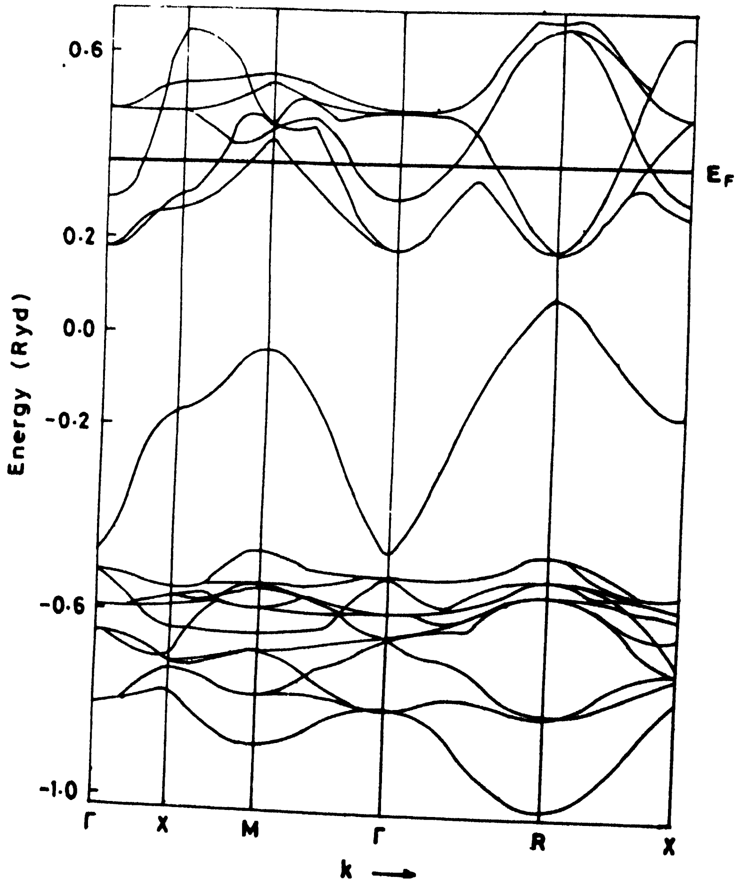

Figure 5. Band structure of $BaPbO_3$ at $\frac{V}{V_0} = 1.0$.

the experimental confirmation for the observed increase in T_c with pressure is yet to come. We have to admit here the problems and certain uncertainities faced in calculating $\langle\omega^2\rangle$ of the different species as well as the variation of $<\omega^2>$ with pressure. For elemental solids, the problem was approached by studying the variation of the Gruneisen parameter with pressure (Asokamani *et al* 1986a, 1986b). Here the problem becomes more complicated.

3.3. Electronic energy bands and superconductivity in intermetallics of the type $MgCu_2$. :

3.3.1. Electronic structure and superconductivity of $BaRh_2$ *and* $LaRu_2$:

The first energy band calculations ever made for the intermetallics $BaRh_2$ and $LaRu_2$ are given in Figures 9 and 10 (Asokamani *et al* 1980 and Subramoniam *et al* 1990). These superconducting solids crystallise in Laves phases with $MgCu_2$ structure tupe. Table 5 gives the parameters associated with the calculation of T_c and the agreement between the theory and experiment is found to be good. Apart from $BaRh_2$, $SrRh_2$ and $CaRh_2$ also

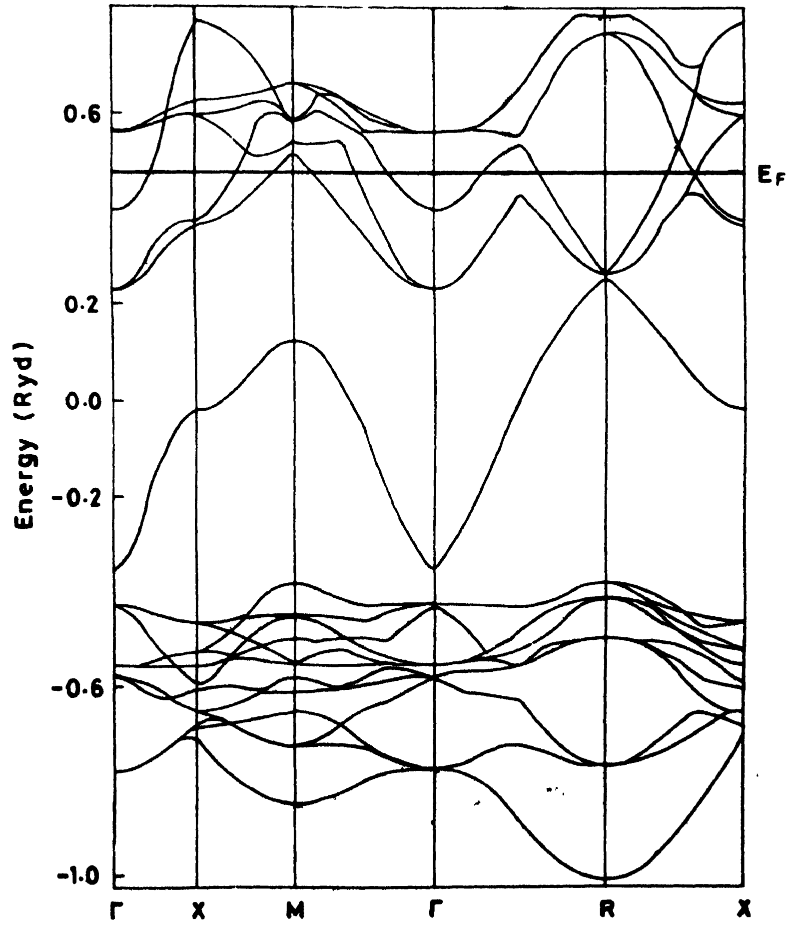

Figure 6. Band structure of $BaPbO_3$ at $\frac{V}{V_0} = 0.9$.

exhibit superconductivity. One of the problems faced here is that the Debye temperature for most of these solids which is needed to calculate T_c are not known. In all these solids, we find a finite *d*-electron contribution which we attribute to be responsible for superconductivity.

Table 5. The values of E_F, $N_l (E_F)$, $\O_l (E_F)$, $D_l (E_F)$, η and λ for $BaRh_2$ and $LaRu_2$.

			$BaRh_2$			$LaRu_2$	
		Ba		Rh			Ru
E_F (Ryd.)			− 0.404			− 0.350	
$N(E_F)$	s	0.119		1.961	0.012		0.673
(states/Ryd/	p	2.248		4.993	3.432		1.899
/cell/spin)	d	0.134		57.853	0.348		81.167
Total			67.311			87.535	
$\O_l(E_F)$	s	0.675		0.767	− 0.860		0.785
	p	0.602		− 1.105	− 0.483		− 1.110
	d	1.354		− 0.048	1.335		− 0.085
$D(E_F)$	s	4.637		− 1.532	3.631		− 1.645
	p	2.304		0.242	− 3.620		0.137
	d	1.242		− 84.601	1.107		− 17.138
η (a.u)		0.036		1.379	0.151		0.112
Total			1.315			0.263	
λ		0.011		0.561	0.045		0.047
Total			0.572			0.092	

3.4. *Electronic structures and superconductivity in AB and elemental solids under high pressure. :*

Energy bands of a number of mono sulphides (Mathi Jaya *et al* 1989c, 1990) and pressure induced superconductivity in elemental solids such as Te, I, Xe and Bi (Asokamani *et al* 1989) were investigated. Superconductivity observed in Te, I and Bi at high pressures have been explained on the basis of their high pressure band structures.

The problem of metallic Xe is quite interesting as it speaks for the predicting capability of band structure calculations. It should be recalled that metallization of Xe was predicted in the range of 1.5Mbar by the band structure calculation of Ross and McMahan (1980) and it was found to be in agreement with the Herzfeld criterion (1927). Metallization of Xe in this pressure range was recently reported by two groups (Goettel *et al* 1989 and Reichlin *et al* 1989). It has been experimentally observed that most of the non metals undergo Insulator-metal transition under pressure and become superconductors under high pressure. We undertook a systematic study of solids in the periodic table which exhibit the above said characteristics.

We worked with Te, *I* and Xe. In the case Xe, we have predicted superconductivity. We performed the band structure of Xe at 1.37 Mbar as the lattice constants *c* and *a* for this pressure were known. The calculated band structure was very similar to the one that was reported recently (Jephcoat *et al* 1987). The calculated value of T_c was around 8.8 K (Subramoniam and Asokamani 1989) and this is yet to be verified experimentally. However we strongly feel not only Xe but other inert gas solids should exhibit superconductivity at high pressures. Our theoretical calculations performed on a large number of elemental solids such as divalent Ba (Subramoniam *et al* 1987), trivalent rare earths Sc, Y and Lu, and non metals such as Te, I etc., show that at high pressures, there is the $s \rightarrow d$ electron transfer which was proposed by Witting (1982). $s \rightarrow d$ electron transfer has been confirmed experimentally also (Syassan *et al* 1981).

4. Correlation between electronegativity and superconductivity

An interesting observation was made with regard to the average electronegativity of oxide superconductors. All oxide superconductors irrespective of the magnitude of T_c were found to have their average electronegativity in the range 2.5 to 2.65 and we lay this as one of the criteria for oxide systems to exhibit superconductivity (Asokamani and Manjula 1989). A correlation between electronegativity of constituent atoms and T_c of superconductors has been established (Balasubramanian and Rao 1989).

Another important aspect of our present work in relation to electronegativity is that we are able to offer an alternate approach to determine the pressures required to drive elements like Ba, Sc, Y and Lu to become superconductors. These pressures evaluated are in very good agreement with what was calculated using first principle band structure calculation and McMillan's formula.

5. Microwave absorption by superconductors

Measurements at microwave frequencies on obsorption and conductivity of superconducting materials can provide information regarding both the normal and superconducting state. Because of this potentiality the study of microwave absorption of $YBa_2Cu_3O_{7-\delta}$ sample has been made. The absorption at 9.5 GHz is determined using cavity perturbation technique. The absorption is studied as a function of temperature in the range 300-85 K. The absorption decreases rapidly at T_c but does not fall to zero value below the transition. The onset transition is at 96 K and the width of the transition is 8 K: The surface impedence of the sample results in the absorption of microwave power and hence even below the transition, in the superconducting state a small absorption results due to London penetration depth. The absorption below transition temperature could also be due to the volume fraction of the sample that does not become superconducting.

6. Results and discussion

The band structure calculations performed on the perovskites of the K_2NiF_4 type structures are unable to bring out the AFM ground state of these oxides. Further, they are unable to open up a gap at the Fermi level. The reason for the failure of the conventional band theory in these cases is, partly, the neglect of magnetic correlations. Attempts are now being made to find improved ways of including these correlations in the construction of potential.

Another observation with regard to the band structure calculations is that in the case of $SrTiO_3$ the LMTO method underestimates the gap. The reason for this lies partly the inherent nature of the local density approximation to the density functional formalism and partly in the use of spherically symmetric potentials in systems where there is high directional bonding. However, Mattheiss (1987) was able to get the gap using the APW method in conjunction with a tight binding pseudopotential fitting procedure. Our calculation on Ba_2PbO_4 which is non magnetic but whose crystal structure is the same as that of La_2CuO_4 is unable to produce the gap, whereas the very recent work of Mattheiss (1990) is able to do so. But it should be understood that it does not come in a single step and in a straight forward way. It is well known that both in A_2BO_4 and ABO_3 structures, the B-O-B interaction is strong as emphasized by the chemical arguments of Goodenough (1971), especially in the ABO_3 compounds. We would therefore like to stress the importance of the incorporation of magnetic interactions as well as directional bonding in these solids (Subramoniam *et al* 1989b).

The proposition that $s \rightarrow d$ electron transfer should be responsible for pressure induced superconductivity has been examined by us in a number of elemental solids and all our band structure results confirm this. The finite *d*-electron number in metallic Xe shown by our calculation has lead us to predict that it should show superconductivity. In the case of $BaPbO_3$ also the *d*-electron number increases under pressure and here also we predict superconductivity. These predictions are yet to be confirmed experimentally. The finite *d*-electron number observed in the intermetallics such as $BaRh_2$, $LaRu_2$ as well as $SrRh_2$ and $CaRh_2$ are used to explain the observed superconductivity. All these studies make us to believe that apart from elemental solids, even in metallic compounds the phenomenon of $s \rightarrow d$ electron transfer should be responsible for promoting superconductivity. This is being investigated.

Even though the present band calculations are unable to bring out the AFM ground state and the band gap, still, as stated by Pickett (1989), there is an overall good agreement between the theoretical density of states and the same obtained from experimental photoemission studies. This shows that the excited state properties could still be studied from band structure calculations.

A striking analogy between NiS_2 and La_2CuO_4 is that both are transformed into metals from AFM insulators under doping. The band structure of NiS_2 as a function of doping or pressure will be carried out soon. The band structures of oxides, sulphides and tellurides which are at the verge of *I-M* transition will be studied theoretically. For most of the systems of the ABO_3 crystal structure type for which we have performed band structure calculations, the theoretical results for the conduction bandwidth, electronic specific heat coefficient, and Pauli paramagnetic susceptibility which have been calculated could not be checked for want of experimental data. The band structure of some of the monosulphides were reported recently (Mathi Jaya *et al* 1990).

A point to be noted while comparison with the experimental results are made is that most of the oxygen perovskites prepared are oxygen dificient. So the oxygen content should be known for the prepared specimen before the respective properties are studied theoretically.

With the present computing system, we have performed the band structures on La_2CuO_4, La_2NiO_4, Ba_2PbO_4, $LaNiO_3$, $BaPbO_3$, $SrCrO_3$, $SrFeO_3$, $SrCoO_3$, $LaRu_2$, $BaRh_2$, $SrRh_2$, $CaRh_2$ and some of the elemental superconductors which become superconducting at high pressures. Since the methodology is known, the band structure of all high T_c systems could be made if the memory and the storage capacity are sufficiently high. Presently, as mentioned earlier, we are concentrating on systems, both magnetic and non magnetic, which are at the verge of *I-M* transition.

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