Properties of solids under high pressure—An electronic band structure approach

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Abstract. The predicting capability of various parameters related to solids by performing their high pressure electronic band structures is discussed in detail. The studies on ground state crystal structure, magnetic structure and magnetic phase transitions under pressures, s – d electron transitions, bulk modulus, Debye temperature, elastic constants, insulator to metal transitions and the phenomenon of pressure induced superconductivity will be discussed with examples. Especially the method of calculating the Debye temperature for a large number of ternary chalcopyrite systems using their recently evaluated band structure will be presented. The limitations of the band theory when used with the local density approximation with respect to the determination of band gaps and magnetic properties will also be discussed.

Keywords. Solids; electronic band approach.

1. Introduction

The evolution of band structure methods have led to considerable amount of understanding of the various properties of materials in the past few decades. The augmented plane wave (APW) method which was proposed by Slater (1937) was one of the widely used methods to calculate the band structure employing the Slater exchange for the contribution of the muffin tin potential. The band structure calculations yield the Fermi energy (E_F) and the density of states at E_F , $N(E_F)$ using which the electronic specific heat coefficient was calculated. Usually this value was compared with the experimental value to check the validity of the method. One of the major steps in the application of band structure to study the mechanical property such as the bulk modulus was performed by Moruzzi *et al* (1978) for several elemental solids using the KKR method. These calculations were extended by Papaconstantopolous (1986) for evaluating their superconducting transition temperatures. Papaconstantopolous *et al* (1977) have also used the APW method in the systematic study of the band structure of a number of elemental solids which also included the spin polarized calculations of some of the ferromagnetic metals.

The introduction of linear methods by Andersen (1975) is a major breakthrough in the calculations of band structures as it vastly reduces the computational time and they are also self consistent although self consistency can be achieved by other methods. Skriver (1984, 1985) adopted the linear muffin tin orbital (LMTO) method for calculating the total energy for different metals in the periodic table and it has improved our knowledge with regard to the correlation between the d electron number and crystal structural stability. The total energy

calculations were performed in a similar manner using pseudopotential method by Cohen for some of the semi-conductors. Thus the band structure calculations even performed under ambient conditions can be used to calculate quantities such as the electronic specific heat coefficient (γ), the Pauli spin susceptibility (χ_p) and the electronic charge density distribution as well as their momentum distribution in solids (Mijnarends 1973).

In 70's with the advent of high pressure diamond anvil devices Wittig and Probst (1978) studied the phenomenon of pressure induced superconductivity in several metals. Experimental observations with regard to crystal structure modifications, the phenomenon of insulator–metal transition, superconductivity as well as magnetic phase changes at high pressures have been made for a large number of systems. The band theory has reached such a high level of sophistication so as to enable the study of all the above mentioned phenomena. In this paper we shall discuss certain case studies which are of recent origin.

2. Superconductivity in ionic solids

One of the most exciting experimental observations which has been currently reported is the superconductivity in an ionic solid such as CsI (figure 1) and the same was predicted by us from band structure calculations as early as 1991 (Asokamani *et al* 1991; Eremets *et al* 1998). The result is of fundamental importance because of the fact that till date the only other ionic solid in which superconductivity is said to have been observed is NaCl. Pressure induced superconductivity is very well known in metals, semiconductors and van der Waals solids (figure 2). The existence of certain systematics lead to

the question as to 'why superconductivity was not observed in ionic solids?' and this has been raised earlier (Asokamani *et al* 1997). Pressure induced superconductivity in group III transition metals Sc, Y and La and as well as in other groups show the general trend viz that the pressure required to drive a material to go to the superconducting state (P_s) depends upon the radius of the atom. As the atomic radius decreases the pressure required P_s for the onset of superconductivity increases. Further the group IV elements C, Si, Ge, Sn, Pb are of considerable significance as it nicely shows insulator-metal transition. The last two elements are superconductors with their T_c values decreasing with their atomic radii and similarly the metallization pressures (P_M) and the superconducting pressures for Ge and Si increase with their atomic radii. Further diamond is expected to become metallic at any moment and the trend clearly shows that it should also become superconducting at very high pressures.

It is important to note that there exists a correlation between metallization pressure and atomic radius as was shown by the theoretical calculations of McMahan (1986) for the van der Waals solids also. This correlation relating metallization and superconducting pressures with atomic radii really indicate their connections with the lattice vibrational frequencies or the Debye temperature.

The predicting capability of band structure calculations has been very good with regard to crystal structural transformation and metallization but not with respect to superconducting transition temperature. The calculation of T_c as well as its variation with respect to pressure are somewhat complicated. The factors affecting T_c have been discussed in detail elsewhere (Asokamani *et al* 1986) and are discussed briefly here which agrees with

the experimentalists who have observed a T_c of 2 K at 1.8 Mbar in CsI and the suggested uncertainties in the calculations.

3. Phase transformation under pressure

Before superconductivity occurs the ionic solids should become metals and earlier to this they undergo structural transformations. Most of the alkali iodides usually are transformed from B1 phase (NaCl structure) to B2 phase (CsCl structure). The transformation pressures or the corresponding reduced volumes are studied by performing total energy calculations. The total energy of the solid is given by the following expression:

$$E_{\text{tot}} = T_{\text{kin}} + \sum_R U_R + \sum_R \sum_{R'} Z_R Z_{R'} \sum_T |R - R' - T|^{-1},$$

where the first term is the kinetic energy of the valence electrons which should be expressed as the difference between the total energy and the potential energy of the non-interacting electrons. In atomic sphere approximation, therefore

$$T_{\text{kin}} = \int_0^{E_F} E N(E) dE - \sum_R \int_0^{S_R} \int_0^{n_R} v_R(r) n_R 4\pi r^2 dr,$$

where $N(E) = \sum_{R1} N_{R1}(E)$ is the sum of the projected density of states, $v_R(r)$ is the one electron potential in the sphere at R and $n_R(r)$ is the spherically averaged charge density. The second term is the sum of the intra-sphere interaction energy between the electrons themselves and between the electrons and the nucleus in that sphere.

Figure 1. Pressure induced superconductivity in CsI.

Figure 2. Pressure induced superconductivity in metals.

The TBLMTO calculations performed by us show the expected transformations as shown below in the case of RbI and KI whereas CsI already exists in the B2 phase at ambient pressure. Figure 3 shows the structural transformation in the case of RbI whereas in table 2, the theoretical reduced volumes are compared with the experimentally quoted values.

There is a continuous $s/p \rightarrow d$ electron transfer in all solids under pressure. The continuous increment in the d electron number is one of the factors, which will promote superconductivity in all solids, and the manner in which d electron number is increasing as a function of pressure is shown below (table 1) in the case of CsI. The other factors which influence superconductivity are discussed below.

4. Factors affecting T_c

First of all the McMillan's formula which has been used to calculate T_c has got an exponential dependence on the electron-phonon coupling constant λ thus making T_c to be very sensitive to λ as shown below:

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

where

$$\lambda = \frac{\eta}{M \langle \omega^2 \rangle},$$

η is the electronic parameter which involves the Fermi energy E_F , the density of states at E_F , $N(E_F)$, the wave functions and their derivatives calculated at E_F and corresponding to the Wigner-Seitz sphere radius. These parameters which determine η are all calculated system-

atically as function of pressure, whereas the variation of phonon frequency with pressure could not be calculated in the same manner. In other words, the phonon part is not calculated in a rigorous manner as that of the electronic part. Soft modes could have occurred during structural transformations and it is a difficult problem to calculate $\langle \omega^2 \rangle$ variation with pressure.

However, we, using the Gruniesen constant variation in the case of La, made an attempt in this direction which did improve the calculation of T_c (Asokamani *et al* 1986). Further the variation of θ_D as a function of temperature and pressure should be known as it occurs as a pre factor in the McMillan's expression. Because of the above said factors the theoretical calculations can at best give only the trends in the variation of T_c with pressure. Theory has seldom been ahead of the experimental observations. At this juncture it should be said that the theoretical prediction viz CsI will become a superconductor under pressure is indeed a remarkable success of the band theory.

In spite of the above mentioned limitations with regard to the calculation of T_c , which mainly arise because of the McMillan's equation, still the band theory has been extremely successful in predicting the structural transformations as well as insulator-metal transition in general. In the case of the other alkali iodides the pressure corresponding to structural transitions and insulator-metal transition are given in table 2 and are compared with the experimental results (Mercy Amirthakumari *et al* 1997).

The systematics discussed so far show that irrespective of the nature of the bonding, the solids undergo the following sequence under pressure: crystal structural transformation, loss of covalency or ionicity, IMT and

Figure 3. Total energy as a function of volume in RbI in B1 and B2 structures.

Table 1. Density of state at Fermi energy (no. of states/Ry./cell) and the angular momentum decomposed charge distribution (no. of states in electrons/atom) in CsI at different reduced volumes.

V/V_0	$N(E_F)$ (States/Ry.)	No. of states		
		n_s	n_p	n_d
0.500	0.023	1.2	5.5	0.6
0.450	0.107	1.19	5.4	0.7
0.425	0.125	1.19	5.3	0.75
0.400	0.467	1.18	5.2	0.85
0.325	7.210	1.2	5.0	0.95
0.300	8.403	1.2	4.75	1.10

Table 2. Metallization volume ratios and the corresponding pressure (in GPa) given in parenthesis.

Compound	Present work	Expt.	Herzfeld
RbI	0.365(122.3)	0.45(85)	0.363
KI	0.350(154.9)	0.45(115)	0.376

superconductivity. CsI is isoelectronic with that of BaTe and Xe and the possibility of superconductivity has been already discussed (Subramoniam and Asokamani 1989). Since the ionic solid CsI has become a superconductor, CsBr, CsCl and CsF should also become superconductors under pressure and the pressures required to drive them to go to the superconducting state should be large as the radii of the halide ions are becoming progressively smaller. These studies make us to suggest that all ionic solids should become superconductors at high pressures. Further diamond which is expected to become metallic at any time should also ultimately exhibit superconductivity. The one difference which we have observed with regard to metallization and superconductivity in covalent and ionic solids is that in the former class $P_M = P_S$ whereas $P_M \neq P_S$ in the latter case. We anticipate that the differences between P_M and P_S should become larger with the percentage of ionicity, as in the case of BaTe vs SnTe.

5. Magnetic transitions under pressure

The discovery of high T_c superconductors led to the investigations of magnetic insulators using band theory. Similar to the study of equilibrium lattice structures, lattice constants, bulk moduli and their crystallographic modifications under pressure, the total energy calculations performed using spin polarized band structure calculations have been able to give successfully the ground state magnetic structure, magnetic moments and magnetic structural transformations. These studies performed in the case of cubic perovskite oxide systems are given below in table 3 (Pari *et al* 1995).

6. Ternary chalcopyrites

The band structure results obtained for a number of ternary chalcopyrites of the ABC_2 ($A = \text{Cu, Ag; B = Ga, In; C = S, Se and Te}$) type compounds were used to calculate their bulk modulus. Interrelationships connecting cell volume, bulk modulus and Debye temperature were established for as many as 12 systems and they are given below (Asokamani *et al* 1998).

$$B_0 = -0.075 V_0 + 160.1,$$

$$B_0 = 0.107 \theta_M - 40.059,$$

where B_0 , V_0 and θ_M are respectively the bulk modulus, unit cell volume and melting point. These linear relations are of considerable significance as they are capable of yielding the bulk modulus and melting temperature once the cell volume for any solid crystallizing in this structure is known.

7. Conclusions

From our studies we observe that the band gaps are underestimated because of the local density approximation which is well known in the case of band insulators. Further the kind of exchange—correlations usually used in the one-electron band structure calculations—are inadequate and the calculations are incapable of opening up the expected band gaps in the strongly correlated systems. Yet the band structure results quoted in this paper obtained using the LMTO method or the LAPW method are capable of predicting the correct equilibrium structures, the lattice parameters, bulk modulus, crystal structural modifications and metallization pressures. However, the calculations of superconducting transition pressures are somewhat difficult, due to the factors which go into the McMillans formula. The spin polarized band structure calculations give the correct magnetic ground state, magnetic moments and magnetic phase transitions unless the system is strongly correlated.

Our studies on a large number of pressure induced superconductivity make us believe that diamond will be a pressure induced superconductor and experimentalists

Table 3. Variation of insulating gap (E_g), magnetic moments and the corresponding phases as function of reduced volume (V/V_0) for the system LaMO_3 ($M = \text{Sc, Cr, Fe and Co}$).

LaMO_3	(V/V_0)	Phase	E_g (eV)	Magnetic moment of M ion (μ_B)
LaScO_3	0.95	Insulator	4.807	0.000
	0.90	Insulator	4.941	0.000
	0.85	Insulator	5.087	0.000
	0.80	Insulator	5.167	0.000
	0.75	Insulator	5.093	0.000
LaCrO_3	0.95	AFI*	0.300	2.771
	0.90	AFI	0.145	2.714
	0.85	AFM#	0.000	2.650
LaFeO_3	1.04	AFI	0.541	4.144
	1.02	AFI	0.508	4.151
	0.98	AFI	0.403	4.165
	0.96	AFI	0.359	4.172
	0.94	AFI	0.242	4.172
	0.92	AFI	0.176	4.169
	0.90	AFM	0.000	0.872
	0.88	AFM	0.000	0.862
LaCoO_3	1.10	Insulator	0.349	0.000
	1.05	Insulator	0.330	0.000
	0.95	Insulator	0.514	0.000
	0.90	Insulator	0.541	0.000
	0.85	Insulator	0.594	0.000
	0.60	Insulator	0.152	0.000
	0.55	Metal	0.000	0.000

AFI*, Anti ferromagnetic insulator; and AFM#, anti ferromagnetic metal.

should search for superconductivity in ionic systems as all ionic systems are anticipated to become superconductors irrespective of the numerical values of T_c .

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