

Structural phase transitions and superconductivity in hexagonal tungsten bronzes

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Abstract. The anomalous behaviour of the superconducting transition temperature T_c as a function of x in M_xWO_3 (hexagonal tungsten bronzes), where $M = K, Rb$ or Cs and $0.16 < x < 0.33$, is explained in terms of structural transitions involving WO_6 octahedral chains which are subject to Jahn-Teller (J-T) effect. Above a critical concentration ($x_c \sim 0.24$) there is cooperative J-T effect resulting in a structural transition. Below this, there will exist only local distortions. The effect of these is to modify the density of states and lead to shifting and splitting of the relevant peaks. It is shown that the density of states profile at the Fermi level controls the superconducting transition temperatures as a function of x .

The conduction electrons in these systems are J-T polarons subject to competition between symmetry-breaking distortion and the band delocalizing effects.

Keywords. Hexagonal tungsten bronzes; Jahn-Teller polarons; superconductivity; structural transition.

1. Introduction

Tungsten bronze with the formula M_xWO_3 , where M represents alkali metal ions, constitute a series of non-stoichiometric compounds and exist in several structures as a function of concentration x of M atoms. These range from cubic to tetragonal (I & II) to hexagonal (Kihlberg 1983). In the present paper, we shall be interested only in hexagonal tungsten bronzes (HTB) which have $M = K, Rb$ or Cs and x can vary from 0.16 to 0.33. These systems exhibit anomalous electrical and structural properties as a function of x and temperature. The superconducting transition temperature T_c as a function of x displays a minimum around $x = 0.25$ in K_xWO_3 and Rb_xWO_3 and in CS_xWO_3 a smooth lowering of T_c on going from $x = 0.20$ to $x = 0.32$ (Stanley *et al* 1979; Skokan *et al* 1979; Cadwell *et al* 1981). The resistivity as a function of temperature shows a local minimum at a temperature T_B (in the temperature range 100 to 300 K) in both K_xWO_3 and Rb_xWO_3 . The value of T_B varies with x . In fact, T_B peaks at the value $x = 0.25$. The Hall and Seebeck coefficients exhibit similar high temperature anomalies (Stanley *et al* 1979; Cadwell *et al* 1981). These anomalies, which depend on the concentration of alkali atoms, suggest some kind of structural phase transitions and phonon softening. Although earlier experimental work using x-ray diffraction did not reveal any clear-cut structural transition, recent neutron diffraction measurements do show evidence of these in Rb_xWO_3 as well as softening of some phonon modes (Sato *et al* 1982, 1983). In order to understand the nature of these phase transitions in HTB, it is essential to have an idea of their structure.

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2. Structure of HTB

In these systems, an arrangement of corner sharing WO_6 octahedra provides the main framework of the structure (Magneli 1953; Kihlborg 1983). The packing is such that they leave triangular and hexagonal cages or tunnels (see figure 1). The alkali atoms (M) reside in the hexagonal cages (size about 2 Å). The triangular cages are rather small. At concentration $x = 0.33$ there are two M atoms per unit cell and all cages are filled. For $x = 0.16$ there will be only one M atoms per unit cell (50% of hexagonal cages vacant). The electron diffraction and microscopy results on K_xWO_3 by Bando and Iijima (1981) show incommensurate superstructure along the c -axis for $0.24 < x < 0.26$ at room temperature suggesting approximate doubling of the c axis. However, the important point to note is that the original c itself extends over two octahedral layer which is caused by a slight displacement of the W atoms in the HTB structure.

Results of neutron diffraction studies by Sato *et al* (1982) on $\text{Rb}_{0.27}\text{WO}_3$ at 10 K show additional peaks which disappear in the high temperature phase above $T_S = 205$ K. This temperature T_S is in agreement with the temperature T_B connected with resistivity anomaly. The sub-lattice peaks are explained by the ordering of Rb atoms in the c -axis which leads to the doubling of this axis. Yet another ordering of Rb atoms, this time in the c -plane, occurs in the samples with $x < 0.25$. This appears at temperature T_S , which varies from 480 K to 280 K as a function of composition (Sato *et al* 1983).

Perhaps the most important transition observed by this group is the one at 420 K and in the range $0.25 < x < 0.33$ associated with the appearance of (103) reflection. The peak is absent above 420 K. Below this temperature, a softening of the optical phonons at the Γ point takes place. The transition is associated with the distortion of the WO_6 octahedra and is nearly of second order (Sato *et al* 1983). We believe that of the three structural transitions described above, the last one is of crucial importance in determining the superconducting behaviour in these systems. The distortion arises from a Jahn-Teller (J-T) type splitting of the atomic t_{2g} levels of the W atoms.

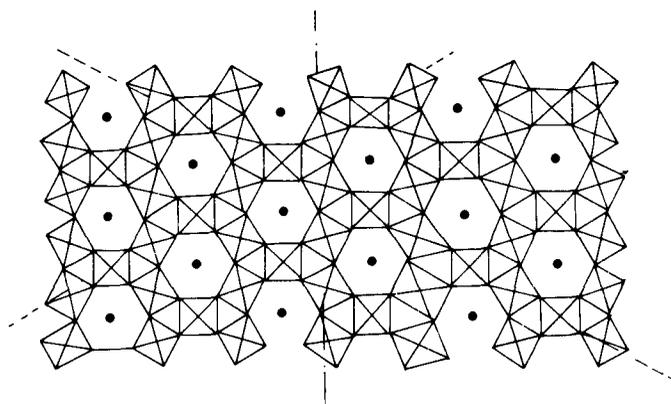


Figure 1. The structure of hexagonal tungsten bronzes (M_xWO_3). The squares represent WO_6 octahedra which share corners. Alkali metal ions (M) are denoted by dots which reside in the hexagonal cages (After Kihlborg 1983). For $\text{Rb}_{0.27}\text{WO}_3$, the lattice constants are $a = 7.38$ Å, $c = 7.56$ Å with space group $D_{6h}^2 - c6/mcm$ (Magneli 1953).

3. The role of J-T effect on the electronic structure and phase transitions

Some authors (Stanley *et al* 1979; Cadwell *et al* 1981) believed that alkali metal ions are mainly responsible for the anomalous electronic properties of these systems. Indeed, the idea was mooted whether the transition of the high temperature uncorrelated to low temperature correlated motion of alkali metal ions in the hexagonal channels might provide a possible mechanism. Along this theme a few workers (Ngai and Reinecke 1978; Vujicic *et al* 1981) had invoked interaction between electrons and local structural excitations in the phase transition regions. This new interaction will give an additional superconductivity pairing mechanism. But this mechanism can be important only when the temperature of the structural phase transition T_S is close to the superconducting transition temperature T_C .

We have seen earlier that for M_xWO_3 systems, the structural transition temperatures T_S and T_S' are several hundred degrees above T_C which is less than 8 K. It is extremely unlikely that local structural excitations will exist at low temperature (< 10 K). Accordingly, this mechanism can be ruled out for giving anomalous superconducting behaviour. At such low temperatures, the ordering of alkali atoms has already taken place.

The observed softening of the optical phonon mode at the Γ point is much more relevant in that it is related to the distortion of the WO_6 octahedra. However, the corresponding transition temperature T_R (~ 420 K) is again hundred times higher than T_C . Its influence will come through the modulation of electronic density of states because of distortion (induced by J-T effect). To summarize, the central point of our approach is to examine the effect of the concentration-driven structural transition which has already taken place at high temperature on the electronic structure of the systems in question in the low temperature region (< 10 K).

In HTB systems, we have formations of chains of WO_6 octahedra along the c -axis and in the basal plane along three directions which are related to each other by rotation (around the c axis) by 120° . The alkali metal atoms, having donated their valence electron, are in the closed shell configuration. These ions also form linear chain but there will be interruptions when their concentration falls below $x = 0.33$. Their role in the electronic structure of the system is secondary. They may provide Einstein-type modes of vibration (Kamitakahara *et al* 1979) and their ordering will have some effect on the distortion of the lattice. Thus the conduction mechanism and the electronic band structure stem primarily from the WO_6 octahedral chains along the four directions mentioned above. The electronic configuration of atomic tungsten W is (closed shell $+ 5d^46s^2$). In WO_3 , the ionic configuration is $W^{6+}O_3^{2-}$, *i.e.* W ion has lost all its valence electrons. Indeed solid WO_3 is an insulator and there are no free electrons in the conduction band. The conductivity and superconductivity of M_xWO_3 arise from the electrons (one each from each M atom) donated by the alkali atoms to tungsten $5d$ states. In the field of the $6O^{2-}$ ions in WO_6 octahedron, the three t_{2g} orbitals of the W ion will lie lower than e_g . Thus the tungsten $d(t_{2g})$ orbitals in interaction with p_π orbitals of the oxygen ions give rise to the relevant bonding and antibonding orbitals. In HTB crystals, the symmetry is D_{6h}^3 and the t_{2g} orbitals are further slit into the lowest doublet (dxz, dyz) and upper singlet dxy . Thus in the undistorted configuration of WO_6 , the electrons in lowest doublet will exist in a doubly degenerate orbital state. Such an electron in the octahedron WO_6 will be subject to a J-T effect and there is a possibility of cooperative lattice distortion at a critical concentration x of the M atoms (Finch *et al*

1957; Sinha and Sinha 1964). That J-T or pseudo J-T effect leads to distortion and softening of phonon modes has been known in perovskite systems also *e.g.* BaTiO₃, SrTiO₃ (Shukla and Sinha 1966). We believe that the role of J-T effect will be more pronounced in M_xWO₃ system, than Nb₃Sn or V₃Si (as invoked by Labbe and Friedel 1966) owing to a larger electromagnetivity of the oxygen than Sn or Si. In the light of the above, we propose that at and beyond a critical concentration x of M atoms in M_xWO₃, there is cooperative J-T effect which will lead to structural phase transition due to in-phase distortion of octahedra. For incomplete cooperativity, there may be only local distortion at various octahedra. As a consequence of these transitions, we expect splitting or shifting of the lowest conduction band.

The electrons in the HTB are to be treated as J-T polarons (Shukla and Sinha 1966; Höck *et al* 1983). For the electrons moving in the octahedral chains, there are two competing mechanisms. These are the delocalizing effect of the intersite hopping and the localizing effect of the J-T induced electron-phonon coupling.

The Hamiltonian for such a system is

$$H = H_{el} + H_L + H_{J-T}, \quad (1)$$

where H_{el} is the electronic Hamiltonian having the form

$$H_{el} = \sum_{m\sigma} \epsilon_m^0 C_{m\sigma}^+ C_{m\sigma} + \sum_{m \neq n, \alpha\alpha'} t_{mn}^{\alpha\alpha'} (C_{m\sigma}^+ C_{n\alpha'\sigma} + \text{h.c.}), \quad (2)$$

the Jahn-Teller term

$$H_{J-T} = -A \sum_{m\sigma} Q_m (C_{m1\sigma}^+ C_{m1\sigma} - C_{m2\sigma}^+ C_{m2\sigma}), \quad (3)$$

and H_L denotes the lattice Hamiltonian which includes the coupling between the J-T active vibrational coordinates between different sites. Here $C_{m\sigma}^+$ ($C_{m\sigma}$) represents creation (annihilation) operators for electrons of spin σ in a Wannier state at site m and in the doubly-degenerate orbital ϕ_α ($\alpha = 1, 2$); Q_m refers to the local (symmetry-breaking) J-T active vibrational coordinate. A is the coupling coefficient.

When this coordinate takes a value $\langle Q_m \rangle$, which is non-zero, the term H_{J-T} leads to a local distortion around the electron. In fact H_{J-T} then provides an effective potential. For strong coupling A , the electron may become trapped and the composite J-T polaron moves as a new entity through the lattice of WO₆ chains. Thus depending on the strength of A the electronic motion may vary from a diffusive motion to a coherent band motion.

In the present paper, we shall not discuss the quantitative aspects of the J-T polarons in HTB systems. Instead, we shall examine the features of the band structure of HTB in the undistorted phase and then draw qualitative conclusion of the changes that can arise on taking into account the J-T mechanism.

The orientations of the two degenerate orbitals dxz , dyz of each W ions in the HTB structure is such that there is greater overlap between identical orbitals along the c -direction than overlap between two different orbitals of W atoms in the basal plane. Accordingly, we expect a larger hopping integral along the c -direction than in the basal plane where each tungsten is surrounded by three equivalent neighbouring tungsten sites.

Tight-binding approximation with nearest neighbour W-W interaction gives the

dispersion relation

$$E(\mathbf{k}) = E'_0 - 2t_1 \cos \frac{a}{4}(k_x - \sqrt{3}k_y) - 2t_2 \cos \frac{a}{4}(k_x + \sqrt{3}k_y) - 2t_3 \cos \frac{a}{2}(k_x) - 2t_0 \cos \frac{c}{2}k_z, \quad (4)$$

where a and c are lattice constants defining the unit cell, (k_x, k_y, k_z) are wave vectors in the cartesian directions and t_0, t_1, t_2, t_3 are the magnitudes of the transfer integrals along the c -axis and the three directions along the WO_6 chains in the basal plane respectively. For the undistorted situation we have $t_1 = t_2 = t_3$ and the above dispersion relation is invariant under rotation by $n\pi/3$, (n integer) around the c -axis. We believe the minimum of the band structure lies at the Γ point *i.e.* $(0, 0, 0)$ of the Brillouin zone (BZ). Further t_0 is much larger than t_1 etc owing to large end on overlap of the orbital functions along the c -axis than those in the basal plane. Accordingly, we expect a narrow band in the hexagonal plane of the BZ. We shall not go into the details of the band structure and the concomitant density of states as it will be discussed elsewhere (Ranninger and Sinha 1985). We shall summarise the salient features.

For small wave vectors the dispersion in the basal plane is isotropic but with its increasing magnitude the Fermi surface approaches a hexagonal shape. Near the zone boundary the anisotropy in the dispersion becomes very dramatic. Along the k_x direction the electron energy drops monotonically to zero. On the otherhand in the k_y direction it increases slightly, goes through a maximum and then approaches the BZ in a fairly flat manner.

There is a logarithmic singularity in the density of states arising from the flat portion of the electron dispersion for wave vectors $k_\rho \sim k_\rho^0$ at the zone boundary (note the dispersion was written in cylindrical coordinates, $k_x = k_\rho \cos \phi$, $k_y = k_\rho \sin \phi$). A small anisotropy in the dispersion will wash out this singularity giving rise to a narrow peak centred around the energy value

$$\varepsilon_0 = Bk_\rho^{02}/2, B \text{ being a constant.}$$

The electronic density of states increases as $\varepsilon^{1/2}$ for small energies but above ε_0 it decreases as $1/\varepsilon^{1/2}$. The reason is that the dispersion in the basal plane is rather flat compared to the dispersion along the c -direction.

For small values of the energy ε we have a dispersion of the form $\varepsilon_{\mathbf{k}} \propto t_0 k_z^2 + t_1 k_\rho^2$, and hence the density of states is proportional to $\varepsilon^{1/2}$. When ε is around ε_0 all the states in the basal plane have been filled. Beyond this only states with k -vectors in the c direction are available. In this range the system would reflect a quasi one-dimensional density of states which will fall off as $1/\varepsilon^{1/2}$.

Let us now consider the effect of the phase transition as the concentration of alkali metal ion varies. In effect, this leads to the change in the number of electrons in the WO_6 chains. The phase transition involves mainly the distortion of the octahedra and the order of M atom. As remarked earlier, in our view, it is the first which produces the dominant effect on the dispersion relation and the density of states. The distortion will alter the values of the hopping integrals which will lead to a shift of the bottom of the band and the density of states curve may expand or contract (depending on the directions of change of the lattice deformation). The two densities of states, *i.e.* before and after the concentration-dependent phase transition are sketched in figures 2a and

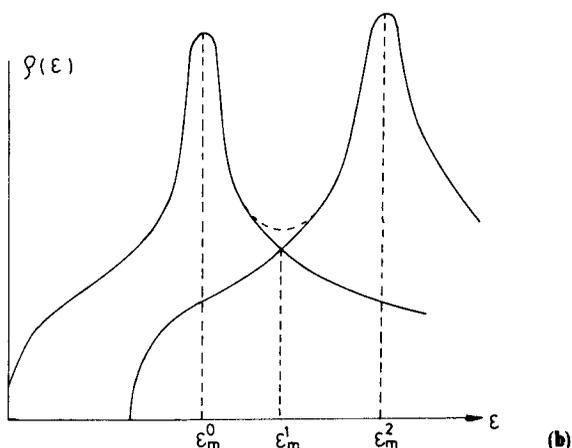
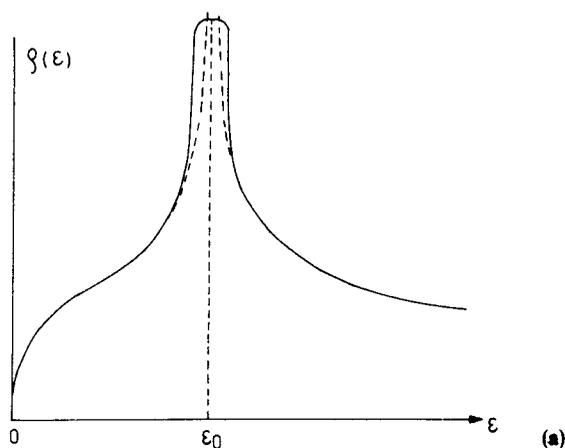


Figure 2a. Density of states $\rho(\epsilon)$ as a function of ϵ for HTB in the undistorted phase (dashed curve). The solid line gives the situation after smoothening the peaks due to distortion.

Figure 2b. Density of state profile for HTB undergoing a cooperative J-T effect above a critical concentration x_c . A superposition of two density of states profile of the type given in figure 2a before and after the structural transition. The rounding off (dashed portion) is expected for realistic density of states.

2b. When the two situations are taken together, a realistic density of states profile will have the following behaviour as a function of x . It will have one pronounced hump followed by a minimum and then rise again to a second hump. The precise form of this behaviour will depend strongly on the size of the substituted alkali metal ions.

4. Superconducting transition temperature

The degrees of J-T induced distortion and cooperativeness vary among the various HTB systems. The structural transition is effected more easily in K containing system than

for Rb and no transition has been observed in Cs system. This is consistent with the picture that smaller the size of the alkali ion in the HTB, the easier it ought to be for WO_3 lattice to distort in conjunction with the J-T splitting.

Now as a function x (hence electron concentration) the Fermi level will explore different regions of the density of states ($\rho(\varepsilon)$) profile. Our stipulation is that the anomalous behaviour in these HTB system arises from the fact that the Fermi level lies around the peak portion of $\rho(\varepsilon)$. Since the peaks are smoothed (see § 3), we can parametrize the relevant part of $\rho(\varepsilon)$ as a series of three parabolic sections, corresponding to a maximum at an energy $\varepsilon_m^{(0)}$, followed by a minimum at $\varepsilon_m^{(1)}$ and a maximum at $\varepsilon_m^{(2)}$ (figure 2b). Thus we can write

$$\rho(\varepsilon) \approx A_l - (-1)^l B_l (\varepsilon - \varepsilon_m^{(l)}), \quad (l = 0, 1, 2), \quad (5)$$

where A_l and B_l are coefficients. We expect that the position of maxima increases as we go from Cs \rightarrow Rb \rightarrow K. We intend to fit the T_c dependence on the electron concentration of these three HTB on the basis of the corresponding variation of density of states at the Fermi level. Accordingly, we have to express the dependence of $\rho(\varepsilon)$ on x , the electron concentration. We have

$$\begin{aligned} x &= \int_0^{\varepsilon_F} d\varepsilon \rho(\varepsilon) = \int_0^{\varepsilon_m^{(0)} + (\varepsilon_F - \varepsilon_m^{(0)})} d\varepsilon \rho(\varepsilon) \\ &\approx \int_0^{\varepsilon_m^{(0)}} d\varepsilon \rho(\varepsilon) + (\varepsilon_F - \varepsilon_m^{(0)}) \rho(\varepsilon_m^{(0)}) \\ &= x_m^{(0)} + (\varepsilon_F - \varepsilon_m^{(0)}) \rho(\varepsilon_m^{(0)}); \end{aligned} \quad (6)$$

$x_m^{(l)}$ corresponds to $\varepsilon_m^{(l)}$ and ε_F is the Fermi energy. Thus

$$\begin{aligned} \rho(\varepsilon_F) &\approx \rho(\varepsilon_m^{(l)}) - (-1)^l \frac{1}{2} (\varepsilon_F - \varepsilon_m^{(l)})^2 \rho''(\varepsilon_m^{(l)}) \\ &= \rho(\varepsilon_m^{(l)}) - (-1)^l \frac{1}{2} \left(\frac{\rho''(\varepsilon_m^{(l)})}{\rho^2(\varepsilon_m^{(l)})} \right) (x - x_m^{(l)})^2. \end{aligned} \quad (7)$$

The expression of the transition temperature T_c (see Sinha 1978) is

$$T_c = W_c \exp[-1/\lambda_{\text{eff}}], \quad (8)$$

where W_c is the energy cut-off in temperature units and

$$\lambda_{\text{eff}} = \rho(\varepsilon_F) V, \quad (9)$$

V being the effective electron-electron interaction constant. Our assertion is that the changes in density of states (which is split due to phase transition driven by concentration-dependent cooperative J-T effect) determines the behaviour of T_c in these systems, with V showing no appreciable change. Thus we reexpress λ_{eff} as

$$\lambda_{\text{eff}} = [\alpha_l - (-1)^l \beta_l (X - X_m^{(l)})^2], \quad (10)$$

where the coefficients have absorbed the interaction constant V also; hence α_l , β_l are dimensionless numbers. Using expressions (8) and (10) we have calculated the transition temperature T_c by evaluating the parameters α_l and β_l for the positions of the extrema in $X_m^{(l)}$. The calculated T_c along with the experimental results are shown in figure 3. For K_xWO_3 the splitting *i.e.* spacing between the two peaks in $\rho(\varepsilon)$ is maximal.

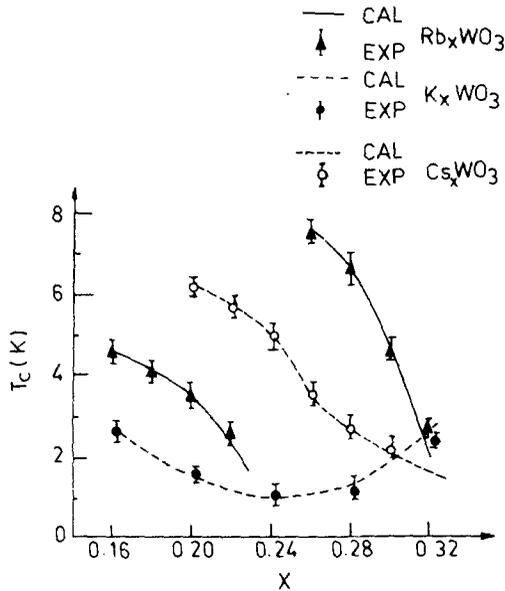


Figure 3. Superconducting transition temperature T_c as a function of concentration in $M_x\text{WO}_3$. The parameters for calculation are
 K_xWO_3 : $W_c = 150 \text{ K}$, $\alpha_m^{(1)} = 0.20$, $\beta_m^{(1)} = 7.15$, $x_m^{(1)} = 0.24$.
 Rb_xWO_3 : $W_c = 115 \text{ K}$, $\alpha_m^0 = 0.3086$, $\beta_m^0 = 13.875$, $x_m^0 = 0.16$, $\alpha_m^{(2)} = 0.3663$, $\beta_m^{(2)} = 36.0625$, $x_m^{(2)} = 0.26$.
 Cs_xWO_3 : $W_c = 170 \text{ K}$, $\alpha_m^0 = 0.3020$, $\beta_m^0 = 11.5$, $x_m^0 = 0.20$, $\alpha_m^{(1)} = 0.22$, $\beta_m^{(1)} = 7.25$, $x_m^{(1)} = 0.33$.

The relevant portion of $\rho(\epsilon)$ being essentially between the two maxima. For Rb_xWO_3 the two maxima lie fairly close together—the region of the minimum being too small—the transition being sharp. For Cs_xWO_3 the band splitting is undetectably small and the density of states are parametrized by a parabolic maximum decreasing towards a distant minimum. The agreement between calculated curves and the observed trend of T_c as a function of x is reasonably good.

5. Concluding remarks

The foregoing analysis of the experimental results and the proposed model for HTB systems suggest the following picture.

The concentration of conduction electrons in $M_x\text{WO}_3$ can be varied over a wide range by doping with alkali metal atoms (M). The principal role of these atoms is to donate their valence electrons to the WO_3 network which provides the conduction channels. Owing to doubly degenerate orbital states of these donated conduction electrons in WO_6 octahedra, they are subject to a J-T distortion. This becomes cooperative above a critical concentration x_c (~ 0.24) of M atoms leading to a structural phase transition. This is indeed supported by neutron scattering experiments which show the appearance of superlattice reflections above a critical concentration. These reflections arise from the deformation of the WO_6 octahedra along with the softening of an optical phonon mode (Sato *et al* 1983).

The structural transitions (whether ordering of M atoms or the superlattice formed by distortion of octahedra) occur at temperatures very much higher than the superconducting transition temperature. Thus the mechanism based on local structural excitations (Vujicic *et al* 1981) cannot hold good as these are frozen out. The J-T induced distortions do, however, provide a self-consistent potential in which the electrons move. The situation is akin to a polaron. In the present case we are dealing with a J-T polaron which is associated with a symmetry-breaking vibrational mode of the complex (Shukla and Sinha 1966; Höck *et al* 1983). When cooperativity is complete above a critical concentration, there is a phase transition which leads to a splitting and shifting of the density of states profiles. When cooperativity is incomplete there will exist local distortions of octahedra. Such random local distortions will smear the peaks in the density of states. The model of the density of states suggested here also provides an explanation of the anomalous transport properties details of which will be given elsewhere (Ranninger and Sinha 1985).

Now a few words about the important modulating role of the density of states at the Fermi level on the superconducting transition temperature. The explicit expression for λ_{eff} is given by

$$\lambda_{\text{eff}} = \frac{\rho(\epsilon_F) \langle I^2 \rangle}{M_{\text{eff}} \langle \omega^2 \rangle},$$

where $\langle I^2 \rangle$ is the average electron-phonon matrix element taken over the Fermi surface, $\langle \omega^2 \rangle$ is the average phonon frequency squared and M_{eff} is the effective mass of the ions in the complex. The renormalized Coulomb interaction μ^* between electrons is negligible in these systems. Varma and Dynes (1976) have demonstrated that in a given category of materials and for the same type of d orbitals involved near the Fermi surface, the quantity $\langle I^2 \rangle / M_{\text{eff}} \langle \omega^2 \rangle$ is approximately constant. Thus the variation of the quantity λ_{eff} in this class of materials is determined exclusively by the density of states at the Fermi level. Our analysis of HTB system supports this correlation between λ_{eff} and $\rho(\epsilon_F)$.

Finally, it should be mentioned that we have taken the situation wherein the conduction band is derived from the antibonding combination of tungsten t_{2g} orbitals and oxygen p_x orbitals. On a J-T induced phase transition the density of states for antibonding states will be pushed up along with a decrease of lattice energy due to distortion involving symmetry-breaking modes which may include anharmonic terms in the quasielastic restoring forces (Pryce *et al* 1965). This leads to an overall lowering of energy after the structural phase transition.

For bonding states density of states would go in the opposite direction. It is desirable to make a detailed band structure calculation invoking (d) orbitals of W atoms and (p) orbitals of the oxygen atoms and determine the detailed nature of the electronic band structure and the corresponding density of states. We believe the shifting and splitting of density of states peaks on phase transition (whether going up or down) explains the behaviour of the superconducting transition temperature. The relevant parameters have to be determined for each situation.

Acknowledgement

One of us (κ ps) should like to thank Dr B K Chakraverty and members of the LEPES, C.N.R.S. Grenoble, France, where this work was carried out for hospitality.

References

- Bando Y and Iijima S 1981 *Acta Crystallogr.* **B37** Suppl. C-303
Cadwell L H, Morris R C and Moulton W G 1981 *Phys. Rev.* **D23** 2219
Finch G I, Sinha A P B and Sinha K P 1957 *Proc. R. Soc. (London)* **A242** 28
Höck K H, Nickisch H and Thomas H 1983 *Hel. Phys. Acta* **53** 237
Kihlborg L 1983 in *Studies in inorganic chemistry* (eds) R Metselaav *et al.* (Amsterdam: Elsevier) Vol 3 p. 143
Kamitakahara W A, Scharenberg R and Shanks H R 1979 *Phys. Rev. Lett.* **43** 1607
Labbe J and Friedel J 1966 *J. de Phys.* **27** 153
Magneli A 1953 *Acta Chem. Scand.* **7** 315
Ngai K L and Reinecke T L 1978 *J. Phys.* **F8** 151
Pryce M H L, Sinha K P and Tanabe Y 1965 *Mol. Phys.* **9** 33
Ranninger J and Sinha K P 1985 to be published
Sato M, Griever B H, Shriane G and Fujishita H 1982 *Phys. Rev.* **B25** 501
Sato M, Fujishita H, Moodenbaugh A R, Hoshino S and Griever B H 1983 *Physica* **B120** 275
Shukla G C and Sinha K P 1966 *J. Phys. Chem. Solids* **27** 1837
Sinha K P and Sinha A P B 1964 *Indian J. Pure Appl. Phys.* **2** 273
Sinha K P 1978 *Indian J. Cryog.* **3** 181
Skokan M R, Moulton W G and Morris R C 1979 *Phys. Rev.* **B20** 3670
Stanley R K, Morris R C and Moulton 1979 *Phys. Rev.* **B20** 1903
Varma C M and Dynes R C 1976 in *Superconductivity in d- and f-band metals* (ed.) D H Douglas (New York: Plenum) p. 507
Vujicic G M, Aksenov V L, Plakida N M and Stamenkovic S 1981 *J. Phys.* **C14** 2377