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Phase transitions in molybdenum sesquisulphide systems between 80 and 600 K

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Abstract. Samples of Mo_2S_3 system and substituted derivatives with Cr, Nb, Cu and Mn have been studied. The resistivity, thermoelectric power, magnetic susceptibility and specific heat indicate clear phase transition at temperatures between 200 and 310 K. X-ray investigations establish the transitions at these temperatures as structural changes. Careful analysis of the data helps to obtain working values for a model for the energy band. Carrier density, effective mass, mobility, band overlap parameter, density of states for the electrons and holes in the overlapping bands at the Fermi level and the band gap for a higher conduction band are obtained.

Keywords. Phase transition; molybdenum sulphide; electrical properties; magnetic properties.

1. Introduction

In recent years several novel phenomena were discovered in oxides and sulphides of transition metals. These have evoked much interest among investigators, *e.g.* metal insulator transitions in V_2O_3 and Ti_2O_3 (Goodenough 1972), high T_c and very high H_c superconduction in MMo_6S_8 (M=Pb, Sn, Ag, Cu, Mg, Zn) (Chevrel 1974, Fischer 1975), charge density waves in layer disulphides TaS_2, NbS_2 (Wilson 1975), a T^2 dependent resistivity extending from 2 to 400 K in TiS_2 (Thompson 1975) and various phase transitions in the structural, electrical, magnetic and other physical properties in many transition metal chalcogenides.

Towards a better understanding of the systems, we have chosen to study in detail a system of samples of Mo_2S_3 and its derivatives $Mo_{2-x}M_xS_3$, M=Nb, Cr, Mn or Cu and x=0·05 to 0·2 (Rastogi 1977). The resistivity ρ, thermoelectric power α, magnetic susceptibility χ, specific heat C_p and x-ray investigations reveal several phase transitions between 80 and 600 K. A detailed analysis of the data, especially the magnetic susceptibility variation with temperature helps to establish a band model and gives fairly convincing values for the band and parameters.

2. Experimental

The compounds could be stabilized by freezing the reactants at 1300 C. X-ray studies ensured homogeneity and crystal structure parameters at room temperature and 110 K revealed phase transitions. Special cryostats and sample holders were designed and operated for resistivity, thermopower, magnetic susceptibility, specific heat and x-ray studies. The measurements showed abrupt changes of slope of the resistivity, magnetic susceptibility and thermopower near 200 K; there is a distortion of crystal structure. The room temperature phase of Mo_2S_3 is monoclinic ($a=6{\cdot}092$ A, $b=3{\cdot}208$ A, $c=8{\cdot}633$ A and $\beta=102{\cdot}43°$) whereas below 200 K from our data taken at 120 K, the crystal has distorted to triclinic with the unit cell parameters ($a=6{\cdot}06$ A, $b=2\times3{\cdot}19$ A, $c=8{\cdot}60$ A, $\alpha=89{\cdot}6°$, $\beta=102{\cdot}5°$ and $\gamma=90{\cdot}3°$). A 'superlattice' transition near 310 K was established from the very weak, low angle lines registered by Debye-Scherrer camera after 24 hours of exposure. The lines could be indexed by using twice the lattice parameters of the original unit cell.

2·1 *Electrical properties*

The room temperature resistivity is $\sim 3\times10^{-3}$ ohm cm. Mo_2S_3 has positive temperature coefficient between 200 and 400 K, indicating semimetallic behaviour. Above 400 K resistivity drops exponentially. The room temperature thermoelectric power is positive, as is the Hall coefficient R_H (de Jonge 1970). With heating, these continue to drop, changing to negative around 400 K. They indicate generation of a *new* set of carriers above 400 K.

2·2 *Magnetic and thermal properties*

The magnetic susceptibility was an invaluable tool to study the nature of this transition metal sulphide with its associated narrow *d*-electron band behaviour. Pure $Mo_{2\cdot06}S_3$ is weakly diamagnetic at 300 K and in units of 10^{-6} emu/cc, $\chi=-0{\cdot}06$; with cooling, χ changed to higher diamagnetic values reaching $-0{\cdot}25$ at 100 K. On raising the temperature, χ *increased* steadily and the compound became gradually paramagnetic above 370 K. Thus Mo_2S_3 shows unusually strong temperature dependence of susceptibility perhaps due to itinerant conduction band electrons and valence band holes. The specific heat curve showed a hump, about 50 K wide, around 190 K and a small peak above 310 K.

For analysis, we divide the discussion as (a) 80–300 K and (b) above 300 K.

2·2 a. *Low temperature range* : Below 200 K, both R_H and α rises rapidly suggesting conduction involving electrons and holes in overlapping bands. The holes are lighter and more mobile than the electrons giving positive α and R_H. With distortion, overlapping bands may cross with reference to each other introducing energy gap near Fermi surface (FS) and exhibit semiconduction (Adler and Brooks 1967). To arrive at some internally consistent values of carrier concentrations (n,p), effective masses (m_e^*, m_h^*), mobility μ and Fermi levels E_f

as function of temperature, we need a prior knowledge of the band structure, the number of carriers, and the dominant mode of scattering. If one type of carriers dominate, the transport equations are easy to handle. Since, at low temperatures, the holes dominate, we assume (i) only holes contribute to thermopower and Hall coefficient, (ii) due to nonstoichiometry in $Mo_{2\cdot05}S_3$, excess electrons exist in the conduction band (CB) over the number of holes in the valence band (VB), (iii) the conduction band is narrow, has high density of states and contributes mostly to magnetic susceptibility; (iv) dominant scattering is due to LO Phonons leading to $\mu \sim \mu_0 T^{-3}$, as found in Ti_2O_3 (Shin *et al* 1973) and $KTaO_3$ (Wemple *et al* 1969); (v) during slow distortion below 200 K density of states at Fermi surface changes rapidly giving less effective electrons and holes at lower temperatures.

2·2 b *Analysis of data*

A. 200 K

Since R_H is $+ 3{\cdot}4 \times 10^{-2}$ cm^3/coul, the concentration of degenerate holes is $1{\cdot}8 \times 10^{20}$/cc. The nonstoichiometry of Mo component (0·06) contributes an excess of $7{\cdot}2 \times 10^{20}$/cc of electrons in the CB and leads, therefore to a ratio, $t = (n/p)$ of $(7{\cdot}2+1{\cdot}8)/1{\cdot}8 = 5$, at 200K.

It was possible to correlate measured values of thermopower, and magnetic susceptibility and Hall coefficient by linear relations over certain temperature ranges and draw out the effective masses, which came to be $\sim 1{\cdot}8$ and ~ 7 for the holes and electrons, respectively.

The susceptibility consists of diamagnetic contributions (for $Mo^{3+} = -15 \times 10^{-6}$ and for $S^{2-} = -40 \times 10^{-6}$ emu/mole) (van Vleck 1932) giving -150×10^{-6} emu/mole or -3×10^{-6} emu/cc. From our plot of χ in terms of $(T/\alpha)^{1/2}$, we got an intercept at $T = 0$ K, representing $\chi_{dia} = -2{\cdot}5 \times 10^{-6}$. This compares, not unfavourably, with our above estimate. From the excess electron in CB, giving Pauli paramagnetic temperature-independent contribution, we estimate $\chi_{para} = + 1{\cdot}5 \times 10^{-6}$ emu/cc. So we estimate a total temperature independent contribution $(-2{\cdot}5+1{\cdot}5)$ *i.e.* -1×10^{-6} emu/cc for later use in our analysis of χ vs T^2.

The temperature dependence of χ can be ascribed mainly to transfer of electrons from valence band to the conduction band with rise of temperature. For our analysis, we proceed with assumptions as follows; (a) hole contribution to χ increases with temperature as electrons are transferred from VB to CB (b) the slope of χ depends on Fermi energy measured from band edge,

$$E_F = \hbar^2/2m^* \ (3\pi^2 n)^{2/3}$$

(c) The density of states, $D(E_F) = [(2m^*)^{3/2}/4\pi^2\hbar^3]$. $E_F^{1/2} = \dfrac{2\ m^*}{4\pi^2\ \hbar^2}\ (3\pi^2 n)^{1/3}$

(d) The paramagnetic susceptibility for holes $\chi\hbar = 2\mu_B^2\ D(E_F)$

(e) For our two band model, $E_F(e)$ and $E_F(h) = (E_0 - E_F(e))$ are measured from corresponding edges of the conduction band and valence band.

(f) We define band overlap ratio, $r = E_F(e) \ / \ E_F(h) = (n_e/n_h)^{2/3}\ (m_h^*/m_e^*)$.

(g) Under our approximation, that at low temperatures holes are much smaller in number than electrons, χ follows a temperature dependence in terms of the susceptibility at 0 K as (Rastogi 1977)

$$\chi_T = \chi_0 \left\{ 1 + \frac{\pi^2}{24} \left(\frac{n_{0e}}{n_{0h}}\right)(1/r^2) \left(kT/EF^0(h)\right)^2 \right\}.$$

We plotted our χ vs T^2, which revealed a slope of 0·65 x 10^{11} emu/cc K^2. Equating it to our above expression, the coefficient of T^2 term then leads to a number for $(n_e/n_h)^{2/3} \times E_F$ (oe)$^{-3/2}$.

Since $n \approx N_D = 7{\cdot}20 \times 10^{20}$/cc at 0 K, the electron band Fermi level at 0 K is calculated as 0·04 eV. This value and effective masses of electrons and holes being utilized as 7 and 1·8, gives the ratio of $(n/p) \simeq 30$, at 0 K. This estimate of $n = N_D$ then gives the value of p and the associated Fermi level is at 0·016 eV giving a band overlap ratio $r = 2{\cdot}5$. Further, a ratio for the density of states $D_e/D_h = (m_e^*/m_h^*)\ (n/p)^{1/3} \sim 12$, is estimated.

B. High temperature range

The ρ, α and χ between 300 and 600 K indicate activated conduction of carriers. The thermopower drops rapidly and changes sign from positive to negative. The χ shows increased paramagnetism at high temperature.

These properties can be understood if there is generation of a *new* set of lighter electrons as temperature rises. Using conventional two-band intrinsic carrier generation expressions, we estimate the position of the effective Fermi level. For the analysis, we assume that the new electrons are more mobile than the holes and determine the variation of resistivity and thermopower above 300 K upto 600 K. However, though the carriers in the valence band give weak temperature-dependent contributions to ρ and α, they, being much larger in number than the lighter electrons, control the susceptibility values at the high temperature ranges.

The mobility is again controlled by LO phonons giving $\mu \sim T^{-3}$. Then resistivity varies as $\rho \sim \rho_0 T^{3/2} \exp(E'_F/kT)$. So plot of log $(\rho/T^{3/2})$ vs $1/T$ would give a value of the Fermi level position with reference to the bottom of the upper conduction band. The thermopower $\alpha_e = (k/e)\ (A - E'_F/kT)$, and could provide supporting value for the Fermi level if we plot α_e vs $1/T$ (Wilson 1953). Indeed, we get near identical E_F, $\approx$ 0·09 eV. Since the magnetic susceptibility of non-degenerate hole gas can be written as $\chi = \chi_0 + (n_p \mu^2{}_B/kT)$, in terms of the high temperature values of n_p = concentration of holes, we get using

$$n_p = 2(m_h\ KT/h^2)^{3/2} \exp -(E_G - E_F)/kT,$$

$$\log\ (\chi - \chi_0)/T^{\frac{1}{2}} \sim (E_G - E_F)kT \qquad (1)$$

Here, χ_0 contains the diamagnetic contribution of the ions and the nearly temperature-independent contribution from electrons in the high density of states band. It is assumed that there is no appreciable change in χ_0 with

temperature. From a plot of equation (1) one obtained $E_G - E_F \simeq 0{\cdot}013$ eV and added to the $E_F = 0.09$ eV, gives, the value of the energy gap, $E_G = 0{\cdot}103$ eV. It is interesting to compare the behaviour of Ti_2O_3 which has transition extending over 200 K centered around 500 K and it changes the low temperature semiconductor phase into a metallic one (Zeiger 1975; Goodenough 1972). Near 500 K, the crystalline c/a ratio has anomalous increase but, contrary to Mo_2S_3, there is no change in the overall crystal symmetry. On the basis of the corundum structure of Ti_2O_3 a 2-band model is proposed (van Zandt *et al* 1968). The energy separations are sensitive to the observed changes of Ti-Ti separation with temparature. This leads to an overlap of conduction and valence bands at high temperature. Mott (1974) conjectured that electrons in narrow conduction bands are probably small polarons and consequently have enhanced mass ($\sim 10\ m_e$). The electrons form a nondegenerate gas; the h^{0}les possibly degenerate, account for high conductivity and positive thermopower and Hall effect. A somewhat similar model for phase transition in Mo_2S_3 would be consistent with our observations.

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