Pramāṇa, Vol. 12, No. 3, March 1979, pp. 269-274, © printed in India

Magnetic susceptibility of mixed valence compounds

ISHWAR SINGH and S K JOSHI
Physics Department, University of Roorkee, Roorkee 247 672

MS received 10 October 1978; revised 27 December 1978

Abstract. Magnetic susceptibility of mixed-valence compounds has been calculated as a function of pressure using Falicov-Kimball model wherein the *f-s* hybridisation has been taken into account. This model can very well explain the continuous as well as discontinuous transitions from ground states of integral to intermediate valence. Our results for magnetic susceptibility are in qualitative agreement with recent experimental results on some mixed-valence compounds.

Keywords. Magnetic susceptibility; mixed valence compounds; Falicov-Kimball model.

1. Introduction

In the recent past much experimental and theoretical work has been done on the phenomenon of mixed-valence (sometimes referred to as intermediate-valence, mixed-configuration, fluctuating-valence or fluctuating-configuration) found in a number of rare-earth compounds (Jayaraman *et al* (1975a, b), Varma (1976), Parks (1977)). These rare-earth compounds undergo continuous (e.g. SmSe, SmTe), as well as discontinuous (e.g. SmS) semiconductor-to-metal transition under pressure (Jayaraman *et al* 1974). Also dopants of smaller ionic radius (e.g. Ce, Pr, Nd, Gd, Tb, Dy, Ho, Y) have been employed to induce the transition in samarium sulfide instead of applying pressure. For example Sm_{1-x} Gd_xS and Sm_{1-x} Y_xS undergo metallic phase for $x \geqslant 0{\cdot}16$ at the atmospheric pressure. At pressure $P=0$ (or $x=0$) *f*-level (containing 6 electrons) is well below the broad $5d$–$6s$ (empty) band (we shall call it *s*-band). As pressure is increased, the gap between *f*-level and *s*-band is decreased (Jayaraman *et al* 1970; Penney and Holtzberg 1975).

The Falicov-Kimball model with and without hybridisation has been extensively used to explain the continuous as well as discontinuous semiconductor-to-metal transition in mixed-valence compounds (Falicov and Kimball 1969; Iglesias Sicardi *et al* 1975; Avignon and Ghatak 1975; Coey *et al* 1976; Goncalves da Silva and Falicov *et al* 1975; Khomskii and Kochrajan 1975; Schweitzer 1978). In this work we use Falicov-Kimball model with hybridisation and calculate static susceptibility at 0°K as a function of the position of *f*-level with respect to the bottom of *s*-band. We find our results to be in qualitative agreement with some recent experimental results of static susceptibility on SmS and Sm $Sb_{1-x}S_x$.

The system is described by the Hamiltonian,

$$H = E_0 \sum_{i\sigma} b^{\dagger}_{i\sigma} b_{i\sigma} + \frac{U}{2} \sum_{i\sigma} b^{\dagger}_{i\sigma} b_{i\sigma} b^{\dagger}_{i-\sigma} b_{i-\sigma}$$

$$+\sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}}\, c^{\dagger}_{\mathbf{k}\sigma}\, c_{\mathbf{k}\sigma} + \frac{G}{N} \sum_{i\mathbf{k}\mathbf{k}'} \sum_{\sigma\sigma'} b^{\dagger}_{i\sigma}\, b_{i\sigma}\, c^{\dagger}_{\mathbf{k}\sigma'}\, c_{\mathbf{k}'\sigma'} \exp\,[i\,(\mathbf{k}-\mathbf{k}').\mathbf{R}_i]$$

$$+\sum_{i\mathbf{k}\sigma} V_{\mathbf{k}i}\,(c^{\dagger}_{\mathbf{k}\sigma}\, b_{i\sigma} + b^{\dagger}_{i\sigma}\, c_{\mathbf{k}\sigma}). \qquad (1)$$

Here $b^{\dagger}_{i\sigma}$ and $b_{i\sigma}$ are the creation and annihilation operators for an electron of spin σ in the localized f-state at ith site with energy E_0 and intra-atomic coulomb correlation energy U. $c^{\dagger}_{\mathbf{k}\sigma}$ and $c_{\mathbf{k}\sigma}$ are creation and annihilation operators for an electron in the state $\mathbf{k}$ and spin σ in the conduction band with energy $\epsilon_{\mathbf{k}}$. Thus the conduction electrons are assumed to be uncorrelated while the localised f-states are approximated by a non-degenerate Hubbard Hamiltonian with zero configuration width. The fourth term describes the intra-atomic coulomb repulsion between the f- and s-electrons. The last term provides hybridisation between localised and conduction electrons, $V_{\mathbf{k}i}$ being the hybridisation parameter. For localised f-electrons coulomb correlation energy U is very large and therefore we study Hamiltonian (1) in the limit $U \to \infty$. Under this condition Hamiltonian (1) allows only two configurations for f-level (a) ' zero f-electron state ', (b) ' one f-electron state '. Now in the present model the $4f^5$ and $4f^6$ configurations of Sm ion in Sm chalcogenides may be regarded as corresponding respectively to zero f-electron state and one f-electron states. The transformation $U \to \infty$ leaves Hamiltonian (1) unchanged except that the second term is absent and the creation and annihilation operators $b^{\dagger}_{i\sigma}$ and $b_{i\sigma}$ obey the following commutation law (Richmond and Sewell 1968).

$$[b^{\dagger}_{i\sigma},\ b_{j\sigma'}]_+ = (1 - b^{\dagger}_{i-\sigma}\ \ b_{i-\sigma})\ \delta_{ij}\ \delta_{\sigma\sigma'}$$

$$[b_{i\sigma},\ b_{j\sigma'}]_+ = [b^{\dagger}_{i\sigma},\ b^{\dagger}_{j\sigma'}]_+ = 0. \qquad (2)$$

To find out susceptibility firstly we find out an expression for n^{σ}_f (B), the average number of f-electrons per site with σ-spin in the presence of an external static magnetic field B in z-direction. (The effect of B is simply to replace E_0 by $E_{0\sigma} = E_0 - \sigma\,\mu_B\,B$, μ_B being the Böhr magneton). To find out n^{σ}_f, of course we should find out n^{σ}_f and n_c (number of conduction electrons) self-consistently with the condition $(n_c + n_f = 1)$. This we do with the help of the Green function technique (Zubarev 1960). If we consider our system eq. (1) as a collection of independent rare earth impurities and use the Hartree-Fock approximation along with relation (2), it can be easily seen that the Green's functions for the f-electrons as well as for conduction electrons can be written as,

$$\ll b_{i\sigma}\,;\, b^{\dagger}_{i\sigma} \gg = \frac{(1-n^{-\sigma}_f)}{2\pi} \frac{1}{\left[(\omega - E_{0\sigma} - G\,n_c) - \sum_{\mathbf{k}} \frac{|V|^2\,(1-n^{-\sigma}_f)}{(\omega - \epsilon_{\mathbf{k}} - G n_f)}\right.}, \qquad (3)$$

and

$$\ll c_{\mathbf{k}\sigma};\ c^{\dagger}_{\mathbf{k}\sigma} \ll = \frac{1}{2\pi}\ \frac{1}{(\omega - \epsilon_{\mathbf{k}} - G\,n_f)}. \qquad (4)$$

Here we have taken the hybridisation parameter V_{ki} to be **k**-independent. Secondly we neglect the effect of mixing on the conduction band.

Now as the density of states is related with the imaginary part of the Green's function, we can easily write down expressions for $\rho_f^\sigma(\omega)$ and $\rho_c^\sigma(\omega)$, the density of states for *f*-and *s*-electrons respectively.

$$\rho_f^\sigma(\omega) = \frac{\left(1 - n_f^{-\sigma}\right)}{\pi} \frac{\Gamma(\omega)\left(1 - n_f^{-\sigma}\right)}{\left[(\omega - E_{0\sigma} - Gn_c)^2 + \Gamma^2(\omega)\left(1 - n_f^{-\sigma}\right)^2\right]} \tag{5}$$

and
$$\rho_c^\sigma(\omega) = \rho_{oc}^\sigma(\omega - Gn_f). \tag{6}$$

Here $\Gamma(\omega)$ determines the width of the localised level and will be assumed independent of the energy. $\rho_{oc}(\omega)$ is the density of states of the unperturbed conduction band.

Now at 0°K, n_f^σ and n_c can be easily calculated from the following three relations

$$n_c + n_f = 1, \tag{7}$$

$$n_c^\sigma = n_c^{-\sigma} = n_c/2 = \int_{-\infty}^{\epsilon_F} \rho_c^\sigma(\omega) d\omega, \tag{8}$$

$$n_f^\sigma = \int_{-\infty}^{\epsilon_F} \rho_f^\sigma(\omega)\, d\omega. \tag{9}$$

For simplicity we assume constant density of states $1/W$ for the conduction band such that

$$\rho_{oc}^\sigma(\omega) = 1/W \text{ when } 0 < \omega < W, \tag{10}$$

$$= 0 \text{ otherwise.}$$

Then from (7), (8) and (10) we can easily get

$$\epsilon_F = \tfrac{1}{2}\,[W(1 - n_f)] + Gn_f. \tag{11}$$

Now with (9), (5) and (11) we can get the self-consistent equation for n_f^σ,

$$\cot \frac{\pi n_f^\sigma}{(1 - n_f^{-\sigma})} = \frac{-\left\{\frac{W}{2}(1 - n_f) - E_{o\sigma} + G(2n_f - 1)\right\}}{\Gamma(1 - n_f^{-\sigma})}. \tag{12}$$

If external field B is zero, $n_f^{-\sigma} = n_f^\sigma = n_f/2$ so (12) gives

$$\cot \frac{\pi n_f}{(2 - n_f)} = -\,[W(1 - n_f) - 2E_0 + 2G(2n_f - 1)]/\Gamma(2 - n_f). \tag{13}$$

Expression (13) is similar to the expression for n_f obtained earlier by Avignon and Ghatak (1975). The difference being that these workers did not consider the correlation effects and therefore occupation-space contraction factor $[1-(n_f/2)]$ is not present in their expression.

In order to obtain the susceptibility we shall differentiate (12) with respect to B and shall find out an expression for

$$\partial\left(n_f^{\sigma}-n_f^{-\sigma}\right)/\partial B\Big|_{B\to 0}. \quad \text{We get}$$

$$\partial\left(n_f^{\sigma}-n_f^{-\sigma}\right)/\partial B\Big|_{B\to 0}$$

$$=\frac{2\sigma\mu_B/\Gamma}{\left\{\left[(1-n_f)/\left(1-\frac{n_f}{2}\right)\right]\operatorname{cosec}^2\frac{\pi n_f}{(2-n_f)}-\left[\frac{W}{2}(1-n_f)-E_o+G(2n_f-1)\right]\right\}} \tag{14}$$

$$\text{or}\quad \chi=\frac{(2\mu_B^2/\Gamma)}{\left\{\left[(1-n_f)/\left(1-\frac{n_f}{2}\right)\right]\operatorname{cosec}^2\frac{\pi n_f}{(2-n_f)}+\cot\frac{n_f}{(2-n_f)}\right\}} \tag{15}$$

We have analysed (13) and have plotted values of n_f as a function of the position of f-level $\left(\frac{E_0}{\Gamma}\right)$ for various values of the coulomb interaction G/Γ. We see that as a function of the parameter E_0, n_f can vary continuously or discontinuously depending on the value of G. In figure 1, we see that the transition is continuous for $G/\Gamma=1{\cdot}0$ and $2{\cdot}0$ but is discontinuous for $G/\Gamma=3{\cdot}0$. We have calculated susceptibility from (15) and (13) as a function of E_0/Γ for two values of $G/\Gamma=1{\cdot}0$ and $2{\cdot}0$ (given by

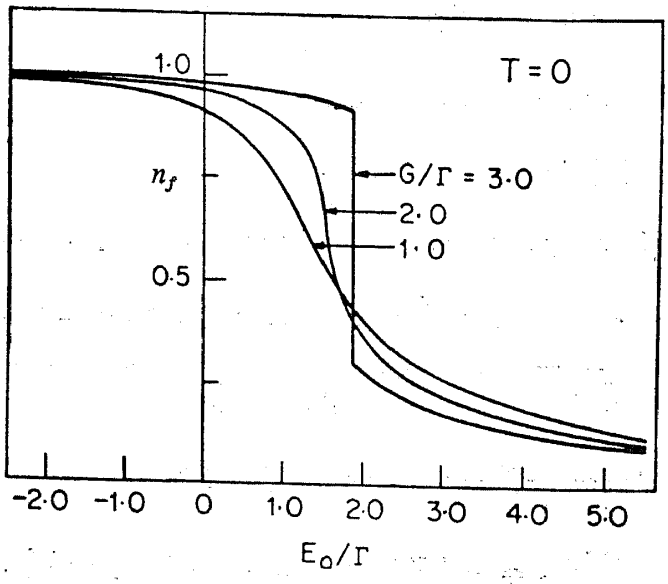

Figure 1. Plot of n_f as a function of E_0/Γ for various values of G/Γ.

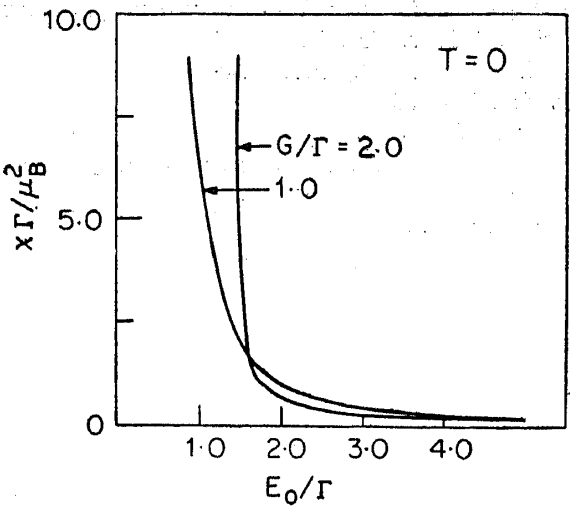

Figure 2. Plot of $\chi\Gamma/\mu_B^2$ as a function of E_0/Γ for two values of G/Γ.

the curves (a) and (b) in figure 2.) Susceptibility for the case $G/\Gamma = 2{\cdot}0$ decreases rapidly with E_0/Γ. Experimentally Maple and Wohllekev (1971) have reported a large decrease in susceptibility of SmS at 6K bar pressure. Qualitatively our susceptibility variation in figure 2b is similar to the experimental behaviour for SmS. At the lower pressures this model does not predict the observed behaviour. It may be due to the assumption that Γ (hybridised f-level width) is independent of the position of f-level E_0. It is obvious that Γ should be large when E_0 is well within the s-band and zero when E is outside the s-band. A better calculation should take this energy-dependent behaviour of Γ into account and that may give correct results in the low pressure region. Susceptibility for $G/\Gamma = 1{\cdot}0$ (figure 2a) shows a variation with E_0/Γ which is qualitatively similar to the experimental result of Beeken *et al* (1978) on Sm Sb_{1-x} S_x, except in the low pressure region.

It can be seen from (15) and (13) that for a set of values of G/Γ such that $n_f = 0{\cdot}774$, susceptibility diverges and hence one had good moment condition. The conduction electrons mediate interaction and lead to a magnetic ground state under this condition (e.g. RKKY coupling, double exchange (Varma 1977)).

References

Avignon M, and Ghatak S K 1975 *Solid State Commun.* **16** 1243
Beeken R B, Savage Wm R, Schweitzer J W and Cater E D 1978 *Phys. Rev.* **B17** 1334
Coey J M D, Ghatak S K, Avignon M and Holtzberg F 1976 *Phys. Rev.* **B14** 3744
Falicov L M and Kimball J C 1969 *Phys. Rev. Lett.* **22** 997
Concalves da Silva C E T and Falicov L M 1975 *Solid State Commun.* **17** 1521
Iglesias Sicardi J R, Bhattacharya A K, Jullien R and Coqblin B 1975 *Solid State Commun.* **16** 499
Jayaraman A, Narayan Murti V, Bucher E and Maines R G 1970 *Phys. Rev. Lett.* **25** 1430
Jayaraman A, Singh A K, Chatterjee A and Usha Devi S 1974 *Phys. Rev.* **B9** 2513
Jayaraman A, Dernier P D and Longinotti 1975a *Phys. Rev.* **B11** 2783
Jayaraman A, Dernier P D and Longinotti 1975b *High Temp. High Pressures* **7** 1
Khomskii D I and Kochrajan A N 1976 *Solid State Commun.* **18** 985
Maple M B and Wohlleken D 1971 *Phys. Rev. Lett.* **27** 511

Parks R D (ed) 1977 *Valence instabilities and related narrow-band phenomena* (New York: Plenum)
Penney T and Holtzberg F 1975 *Phys. Rev. Lett.* **34** 322
Richmond P and Sewell G L 1968 *J. Math. Phys.* **9** 349
Schweitzer J W 1978 *Phys. Rev.* **B17** 758
Varma C M 1976 *Rev. Mod. Phys.* **48** 219
Varma C M 1977 in *Valence instabilities and related narrow-band phenomena* ed R D Parks (New York: Plenum)
Zubarev D N 1960 *Sov. Phys. Usp.* **3** 320