Solid State Communications, Vol. 16, pp. 737–741, 1975. Pergamon Press. Printed in Great Britain

ON THE ANOMALOUS SUSCEPTIBILITY OF SMALL GAP MAGNETIC SEMICONDUCTORS (SmS, SmSe, SmTe)

C. Balseiro, M. Passeggi and B. Alascio

Centro Atómico Bariloche, Instituto de Física "Dr. José A. Balasiro", Comisión Nacional de Energía Atómica, Universidad Nacional de Cuyo, Bariloche, Argentina

(*Received* 16 *April* 1974; *in revised form* 26 *August* 1974 *by A. Pinczuk*)

The magnetic susceptibility of the Sm chalcogenides shows a large dependence on the nature of the anion. In the three compounds (which under pressure become metallic) the energy needed to promote an electron from the $4f$ shell to the conduction band is very small. We present here a mechanism based on the hybridization between f states and band states that relates the anomalies of the susceptibility with the energy gaps.

1. INTRODUCTION

AN INTENSIVE study of Sm monochalcogenides, covering their magnetic, optical and transport properties,[1–8] has been made during the last few years.

Their behaviour under pressure is particularly interesting, because SmS, SmSe and SmTe undergo metal–semiconductor transitions. This takes place discontinuously in SmS at about 6.5/kbar whereas in both SmSe and SmTe the transition is continuous and appears to take place in the range of pressure between 5 and 50 Kbar.

There exist considerable evidence that the transition takes place through promotion of a bound electron from the Sm $4f$ state to a conduction band derived mainly from $5d$ states. In fact, the energy gap between the $4f$ shell and the bottom of the conduction band, is of a few tenths of an eV at zero pressure. The metallic state presents an intermediate valence effects as well as demagnetization of the $4f$ shell, which is probably related to the hybridization of the $4f$ and $5d$ states of the Sm ion. In fact, this hybridization mixes the $4f^6(^7F_0)$ configuration with the magnetic $4f^5(^6H_{5/2})$ and $4f^5(^6H_{7/2})$ configurations of Sm^{3+}, (the effect being larger for smaller gaps), and has been invoked by Maple and Wohlleben[7] to explain the demagnetization of the Sm ions in the metallic phases of these compounds.

In Table 1 we summarize the relevant properties of the compounds under consideration.

The Van Vleck susceptibility at zero temperature of Sm^{2+} is 7.2×10^{-3} e.m.u./mol[9] which accounts for about 75 per cent of the susceptibility of SmS.

Since the splitting between the ground $J = 0$ and the first $J = 1$ states is 421°K in the free ion, and since this value does not change more than about 2 per cent when the ion is submerged in similar crystalline environments[9–11] to those of the chalcogenides, there is a large anomaly in the susceptibility to be explained.[12]

To explain this anomaly, Birgenau *et al.*[9] have proposed an enhancement mechanism based on a phenomenological Heisenberg exchange, which is similar to that proposed by Stevens[1] to account for the g-shift of Gd^{3+} impurities in Sm chalcogenides.

As it can be seen from the table, the susceptibility decreases as the gap increases from SmS to SmTe, and it also increases when the gap decreases by effect of external pressure.

Table 1. Summary of relevant properties of Sm chalcogenides as used in this work

	SmS	SmSe	SmTe
Energy Gap eV	0.20	0.46	0.63
Metal Insulator transition (at room temperature under pressure) kbar	Discontinuous at 6.5	Continuous from 0 to 50	Continuous from 0 to 60
Lattice parameter Å (room temperature)	5.970	6.202	6.601
Susceptibility χ e.m.u./mol	9.47×10^{-2}	7.92×10^{-3}	7.15×10^{-3}
Susceptibility χ (calculated) e.m.u./mol	9.47×10^{-3}	7.87×10^{-3}	7.33×10^{-3}
$d\Delta/dP$ eV/Kbar	0.012	0.0119	0.014
$d\chi/dP$ e.m.u./mol · kbar	172×10^{-6}	73×10^{-6}	10×10^{-6}

In this paper we would like to present a simple mechanism, which could give an important contribution to the excess susceptibility in the insulating phase and is based on the hybridization of the $4f$ levels with the conduction band.

2. MODEL

To calculate the hybridization contributions to the magnetic susceptibility of the Sm monochalcogenides we will use the band structure described by Watcher[6] for the Eu chalcogenides. It includes two empty conduction bands (t_{2g}, e_g) derived from the splitting of the $5d$ states of Sm^{2+} in the cubic crystal field, and localized ionic-like $4f$ states. The bottom of the lowest (t_{2g}) d band falls some tenths of an eV above the energy of the $4f^6(^7F_0)$ configuration of Sm^{2+}.

Since the top of the filled p band is fairly well separated from these levels, we do not consider them in this calculation.

The model Hamiltonian is: $H = H_0 + H_{\text{hyb}} + H_{\text{Zeeman}}$ with

$$H_0 = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}\sigma} C^+_{\mathbf{k}\sigma} C_{\mathbf{k}\sigma} + \sum_{jmm'\sigma} \epsilon_{mm'} b^{j^+}_{m\sigma} b^j_{m'\sigma} + \sum_{j,mm'\sigma\sigma'} b^s_{m\sigma,m'\sigma'} b^{j^+}_{m\sigma} b^j_{m'\sigma'} + \tfrac{1}{2} \sum_{\substack{j,mm'nn' \\ \sigma\sigma' zz'}} J_{\substack{m\sigma mz \\ m'\sigma' m'z'}} b^{j^+}_{m\sigma} b^{j^+}_{m'\sigma'} b^j_{m'z'} b^j_{mz} \quad (1)$$

and

$$H_{\text{hyb}} = \sum_{j,\mathbf{k}\sigma m} (V_{\mathbf{k}m} C^+_{\mathbf{k}\sigma} b^j_{m\sigma} + V^*_{\mathbf{k}m} b^{j^+}_{m\sigma} C_{\mathbf{k}\sigma}). \quad (2)$$

The first term in H_0 represents the energy of the electrons in the conduction t_{2g} band with $C^+_{\mathbf{k}}$ ($C_{\mathbf{k}}$) the corresponding creation (anihilation) operators associated with those states ($\epsilon_{\mathbf{k}\sigma}$ implicity includes the crystal field effects.)

The three following terms are connected with the intratomic structure of the f shell of a given Sm ion in the lattice $b^{j^+}_n$ (b^j_m) being creation (annihilation) operators of an f electron in the j-site with orbital projection $-7 \leqslant m \leqslant 7$ and spin projection σ. The first independent one body operator represents the energy of strongly localized non interacting f electrons moving in the field of the ion core and in the crystal field provided by the other ions in the lattice.

The second (spin dependent) operator represents the spin orbit coupling $h^s_{m\sigma,m'\sigma'} = \langle m\sigma|\xi \mathbf{l} \cdot \mathbf{s}|m'\sigma'\rangle$ within the f shell. Finally the last one, a two body operator, takes into account the interaction among f electrons.

Because of these terms, and due to the strong localization of the $4f$ states, the correlation among these electrons is dominant and leads to a $4f^6(^7F_0)$ Hund's rule state as an approximate ground state of Sm^{2+}.

H_{hyb} takes into account the mixture between the f-orbitals of the Sm ion and the conduction band, under the assumption that the relevant part of these effects can be represented by spin independent one body operators.

H_{Zeeman} represents the effect of a static magnetic field on localized and band electrons.

In a more complete Hamiltonian, one should consider terms involving promotion of two localized electrons either from (a) the same site, or (b) different sites going into the conduction band. We neglected both of them because in case (a) the energy dominator associated with these processes would be too large. In case (b) the corresponding matrix element is proportional to an integral containing two $4f$ states in different sites, which would be very small.

Within the spirit of the Hirst model,[13] we can then imagine for the insulating phase of Sm chalcogenides a set of many electron states that are assumed to be approximate solutions of $H_0 + H_{\text{Zeeman}}$.[1] In this scheme the ground state is given by

$$|\chi_1^{2-} \ldots \chi_N^{2-}; (4f^6\,{}^7F_0)_1 \ldots (4f^6\,{}^7F_0)_N; 0 \ldots 0\rangle$$

where χ_1^{2-} designates a chalcogen 2- ion closed shell (this closed shell being formed by localized orbitals orthogonalized to all other orbitals in any site of the lattice).

The middle part of the set represents the states of the Sm^{2+} ions which have been assumed to be in their ionic (f^6, $^7F_0$) Hund's ground state. The last part indicates the empty t_{2g} band states which obviously, will contain some components of the atomic *ns np* orbitals of the chalcogen ion. These are the Wannier states rather than pure atomic orbitals.

The hybridization term induces an admixture between the approximate ground state and excited states which can be assumed to be of the form:

$$|\chi_1^{2-} \ldots \chi_N^{2-}; (f^6\,{}^7F_0)_1 \ldots (f^5\,{}^6H_{JM})_j \ldots (f^6\,{}^7F_0)_N; 0 \ldots \mathbf{k}_\sigma \ldots\rangle$$

where an f electron from the j-site has been promoted into the k-states of the conduction band leaving in the site j an f^5 shell in the state $^6H_{JM}$.

Taking hybridization as a perturbation, in the presence of magnetic field H, there will be a second order correction to the ground state energy of the form

$$\Delta E^{(2)} = N \sum_{\substack{JM \\ \mathbf{k}\sigma}} \frac{|\langle 4f^6\,{}^7F_0; 0 \ldots 0| \sum_{m\mathbf{k}} V_{\mathbf{k}m} b_{m\sigma}^{+} C_{\mathbf{k}\sigma} |4f^5\,{}^6H_{JM}, 0 \ldots \mathbf{k} \ldots\rangle|^2}{E(4f^5, {}^6H_{JM}) - E(4f^6, {}^7F_0) + \epsilon_{\mathbf{k}} + (\mu_J M + \mu_e \sigma)H} \quad (3)$$

where μ_J is the magnetic moment of the Sm^{3+} ion in the $f^5\,{}^6H_{JM}$ and μ_e is the magnetic moment of the electron in the conduction band.

This contribution has to be added to the terms that lead to Van Vleck and conduction electron susceptibilities. We will here examine this contribution only, because it depends strongly on the gap energy to the conduction band.

Taking into account that $b_{m\sigma}^{+}$ and $b_{m\sigma}$ are double tensor operators, their matrix element within the $4f$ shell states are given by[11,15]

$$\langle 4f^6\,{}^7F_0 | b_m^{+} | 4f^5\,{}^6H_{JM}\rangle = (-1)^{J-5/2} \frac{2J+1}{7}^{\frac{1}{2}} \langle 4f^6\,{}^7F \| b^{+} \| 4f^5\,{}^6H\rangle \times \times \begin{pmatrix} 1/2 & 3 & J \\ \sigma & m & M \end{pmatrix} \begin{Bmatrix} 1/2 & 3 & J \\ 5 & 5/2 & 3 \end{Bmatrix} \quad (4)$$

with the reduced matrix element proportional to a fractional parentage coefficient.[15]

Since the 3-J symbols appearing in equation (4) require that $5/2 \leqslant J \leqslant 7/2$ only these two multiplets of the ^6H term will contribute.

On the other hand, $V_{\mathbf{k}m}$ can be explicitly written in terms of the Wannier functions of the t_{2g} band as

$$V_{\mathbf{k}m} = \sum_{\mathbf{R}_j} \langle f_m(\mathbf{r}) | \hat{h} | d(\mathbf{r} - \mathbf{R}_j)\rangle\, e^{i\mathbf{k}\cdot\mathbf{R}_j} \quad (5)$$

where $d(\mathbf{r} - \mathbf{R}_j)$ are the Wannier functions associated with that band.

The compounds under consideration have the CINa structure. Therefore, using inversion invariance one can show that terms with $R_j = 0$ in equation (5) vanish.[16] Also, due to the strong localization of the $4f$ orbitals, only integrals with the $d(\mathbf{r} - \mathbf{R}_j)$ corresponding to the 12 nearest neighbours Sm^{2+} ions need to be considered.

Using the symmetry operations of the cubic point group (around $R_j = 0$) all these integrals can be related

to the integral of only one of the sites, say: $d(\mathbf{r}-\mathbf{R}_1)$.

The correction to the susceptibility due to hybridization can then be obtained from

$$\chi = -\frac{\partial^2 \Delta E^{(2)}}{\partial H^2}_{H\to 0} = \mu_B^2 \sum_{J=5/2}^{7/2} \Gamma_J \sum_{\mathbf{k}=B.Z.} \times$$

$$\times \frac{5en^2(kx\, b/\sqrt{2})\cos^2(ky\, b/\sqrt{2})}{(\Delta_J + \epsilon_k)^3} \qquad (6)$$

here

$$\Gamma_J = \frac{2^7 \cdot 11}{3 \cdot 7^2} \sum_n \sum_{m'm''} k_{m''}^{m'}(J) \langle f_{m'}|\hat{h}|d^n(\mathbf{r}-\mathbf{R}_1)\rangle \times$$

$$\times \langle d^n(\mathbf{r}-\mathbf{R}_1)|\hat{h}|f_{m''}\rangle$$

and

$$k_{m''}^{m'}(J) = a(J) \sum_{Mm\sigma} \begin{pmatrix} 3 & J & \frac{1}{2} \\ m & M & \sigma \end{pmatrix}^2 (g(J)M + g_e\sigma)^2 \times$$

$$\times [\delta_{mm'}\delta_{mm''} + 2d^3_{mm'}(\pi/2)\, d^3_{mm''}(\pi/2)]$$

b is the lattice parameter and $d^{(3)}_{mm'}(\pi/2)$ are the reduced rotation matrices,[17] $a(5/2) = 1$ and $a(7/2) = 5/2$. $g(J)$ are the corresponding gyromagnetic factors, and $g_e = 2$. The additional index n in $d^n(r - R_1)$ stands to level the three kinds t_{2g} Wannier states.

$$\Delta_J = \Delta + \frac{\lambda}{2}\left(J - \frac{5}{2}\right) \qquad (7)$$

with Δ the corresponding energy gap given in Table 1 and $\lambda = 915°\mathrm{K}$[18] for the spin orbit coupling for the $f^5\,{}^6H$ term.

In equation (6) we take $\epsilon_{\mathbf{k}}$ as resulting from a tight binding approximation for an f.c.c. structure:

$$\epsilon_{\mathbf{k}} = \xi\left(1 - \tfrac{1}{6}\sum_{i\neq j} \cos(k_i b)\cos(k_j b)\right) \qquad (8)$$

with ξ the band width, which we will take as $\xi = 0.6$ eV.

If the choose $\Gamma_{5/2} = \Gamma_{7/2} = \Gamma = 0.19\ 10^{-28}$ erg so as to obtain the total value of χ excess for SmS, and assuming the same value for the other compounds we get the susceptibilities given in Table 1.

From the electrical conductivity measurements reported in reference 4 we then estimate the variation of Δ due to pressure. Using equation (6) and this estimate for $\Delta(P)$ the corresponding variation of susceptibility with pressure can be calculated; the values being also included in the table. The value of Γ taken above to fit the excess susceptibility of SmS is rather large. With this value of Γ the corresponding $\Delta E^{(2)}$ of equation (3) is about 0.4 eV. Thus, if this type of mechanism were the only source for the excess susceptibility the calculation should be improved to avoid the perturbation expansion. However we would like to point out that any other mechanism, involving real or virtual promotion of a $4f^6$ electron into the conduction band[19] should automatically involve the $4f^5$ configuration. Thus a contribution similar to the one presented here would necessarily appear.

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12. As pointed out in reference 7 in order to explain the susceptibility of SmS as a Van Vleck susceptibility, a value of 349°K has to be assumed for the splitting between the $J = 0$ and $J = 1$ states, which implies a change much larger than 2 per cent.

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