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Valence-changing metal–insulator phase transitions

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The example of samarium chalcogenides at $T = 0$ is used to consider the metal–insulator phase transition which alters the valence in rare-earth compounds. It is shown that the s–f Coulomb interaction v and a strong single-site correlation of the degenerate f electrons are accompanied by fairly substantial hybridization of the s–f electrons g. In the semiconductor phase the hybridization produces a new hybrid s band near the f-electron level. Consequently, the valence of the semiconductor phase becomes fractional right down to the lowest temperatures. Depending on the energy parameters, the metal–insulator transition can be of the first order (SmS) or continuous (SmSe, SmTe). In the case of SmS a comparison of the phase diagram with the experimental values of the gap and of the number of the f electrons in the semiconductor phase is used to find the values of g and v.

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1. Extensive studies are being made of rare-earth compounds undergoing —as a result of changes in pressure and temperature— isostructural semiconductor–metal phase transitions accompanied by a change in the valence.[1,2] Typical representatives of such compounds are samarium and ytterbium chalcogenides. For example, in the case of SmS there is a first-order transition accompanied by a considerable change in the volume and valence, whereas in the case of SmSe and SmTe this transition is continuous. The existence of these transitions is attributed to the presence, near the bottom of the conduction band, of a level of localized f electrons which may be transferred to the conduction band on increase in pressure or temperature. The experimental data (for example, measurements of the magnetic susceptibility) indicate that fractional valence is retained right down to the lowest temperatures in the insulator (semiconductor) and metal phases.[2]

A theoretical description of this transition has been developed[3-6] on the basis of the Anderson model[7] supplemented by allowing for the Coulomb repulsion v between the s and f electrons, introduced by Falicov.[8] However, in this description either the wide s band is replaced with a level[3] or no allowance is made for the strong Coulomb repulsion of the f electrons at a single site U, the treatment being restricted[4-6] to the spinless model of the s and f electrons. Moreover, the number of the f electrons n_f is calculated[4-6] using the Green functions of the f electrons obtained on the assumption of the existence of a single impurity with the f level.

In contrast to these earlier treatments,[3-6] we shall make a consistent allowance for the repulsion of the f electrons at a single site. This will result, for example, in a strong dependence of the decay of the f level on the degree of its occupancy. Moreover, we shall assume that the distribution of the rare-earth ions in the crystal lattice is regular. This approach alters the physical picture of the semiconductor state of these compounds, compared with that adopted in the single-impurity approach: the fractional valence is found to be associated with the occupancy of the narrow s band, which appears as a result of hybridization under the f level. In the Appendix we shall use the example of the spinless model to show that our approach differs from the single-impurity treatment also in the quantitative sense: the results obtained in the two cases are identical for the insulator phase only in the limit $g/\Delta \ll 1$ (g is the hybridization constant and Δ is the insulator gap). It is then found that the insulator gap itself can be of purely hybrid nature, i.e., the f-electron level in the insulator phase may lie in the unperturbed conduction band, which is known to be impossible in the single-impurity situation. We shall consider the phase transition in the case of samarium chalcogenides at $T=0$. A comparison of the phase diagram of SmS with the experimental data will be used to estimate the energy parameters of the problem g and v.

2. We shall describe rare-earth compounds using the Anderson–Smith model,[7,9] which allows for the strong repulsion of the f electrons at a single site and for their hybridization with the s electrons. We shall also include the Coulomb interaction between the s and f electrons, which—together with U—is the main mechanism ensuring the feasibility of a first-order transition.

In the case of the Sm chalcogenides, the Sm ion can be either divalent (Sm^{2+}) with the electron configuration $4f^6$ and the total momentum of the shell $J_0=0$, or it can be trivalent (Sm^{3+}) with the configuration $4f^5$ and the total momentum $J=\frac{5}{2}$. Consequently, the hybridization interaction corresponds to the $f^5 \longleftrightarrow f^6$ transitions.

The Hamiltonian of our model is identical with that used earlier[10] to describe the $\alpha-\gamma$ transition in Ce. This Hamiltonian has the form

$$\begin{aligned} H=[\varepsilon_f^{(0)}+v(n_s-n_f)]\sum_n X_{22}^n+\sum_{k,\gamma}\varepsilon_k a_{k\gamma}^+ a_{k\gamma} \\ +gN^{-1/2}\sum_{k,n,\gamma}(e^{-ikn}a_{k\gamma}^+ X_{-\gamma 2}^n+\text{H.c.}). \end{aligned} \tag{1}$$

A rigorous allowance for the strong correlation U of the localized f electrons ($U\sim 5$ eV for Sm—Ref. 11) is made by introducing X operators which change the atomic configurations (for details see Ref. 10). The operator X_{22} corresponds to the atomic configuration f^6 and $X_{\gamma\gamma}$ to the configuration f^5 with the total-momentum projection γ. The number of the f electrons is measured relative to the f^5 configuration, i.e.,

$$n_f=P_2\equiv\langle X_{22}\rangle.$$

The level ε_f is shifted by the Coulomb $s-f$ interaction v relative to the unperturbed level $\varepsilon_f^{(0)}$ and it lies either close to the bottom of the conduction band or inside this band. It is assumed that there are $2J+1$ degenerate conduction bands and that the $s-f$ hybridization affects electrons with the same projections γ of the total momentum.

According to Ref. 12, in the zeroth approximation with respect to $\rho g^2|\varepsilon_f|$ ($\rho=D^{-1}$, where D is the width of the conduction band) the Green function of the s electrons is

$$\left.\begin{aligned} G_{s\gamma}(\omega_n, k)=[i\omega_n-\varepsilon_k+\mu-Kg^2/(i\omega_n-\tilde{\varepsilon}_f)]^{-1}, \\ K=\langle X_{22}\rangle+\langle X_{\gamma\gamma}\rangle={}^1/_6(1+5n_f), \quad \tilde{\varepsilon}_f=\varepsilon_f-\mu. \end{aligned}\right\} \tag{2}$$

In the paramagnetic case considered by us all the matrix elements $\langle X_{\gamma\gamma}\rangle$ are equal and K is independent of γ.

The s-electron spectrum is governed by the poles of the Green function:

$$\varepsilon^{(\pm)}(k)=\frac{\varepsilon_k+\varepsilon_f}{2}\pm\left[\left(\frac{\varepsilon_k-\varepsilon_f}{2}\right)^2+Kg^2\right]^{1/2}. \tag{3}$$

Figure 1 shows the hybridized band scheme for the case when the level ε_f is below the bottom of the unperturbed conduction band. We can see that hybridization shifts this band upward and creates a second band under under the level ε_f.

If G_f and G_s are calculated in higher orders with respect to $\rho g^2/\tilde{\varepsilon}_f$, the level ε_f exhibits decay represented by the constant Γ. In the case of an ε_f level lying in the middle of the wide band, the expression for Γ is[13]

$$\Gamma=\pi\rho g^2(1-K^2)/K. \tag{4}$$

The situation in the insulator phase differs considerably from that considered in Ref. 13 and, generally speaking, it is necessary to solve self-consistent equations for $\Gamma(\varepsilon)$; however, if $K^2\to 1$, the decay can be simply ignored. Before transition in SmS, we have $n_f\approx 0.75$ (Ref. 14) and $\Gamma\approx\rho g^2$. Next, we shall determine the position of the chemical potential with the same precision.

The expression for $G_f(\omega_n, k)$ can be taken from Ref. 12:

$$G_f(\omega_n, k)=K[i\omega_n-\tilde{\varepsilon}_f-Kg^2/(i\omega_n-\varepsilon_k+\mu)]^{-1}. \tag{5}$$

Using Eqs. (2) and (5), we find that at $T=0$:

$$n_f=\frac{K}{2}\sum_k\left(1+\frac{\varepsilon_k-\varepsilon_f}{[(\varepsilon_k-\varepsilon_f)^2+4g^2K]^{1/2}}\right)\theta(-\varepsilon^{(-)}(k)+\mu), \tag{6a}$$

$$n_s=\frac{(2J+1)}{2}\sum_k\left(1-\frac{\varepsilon_k-\varepsilon_f}{[(\varepsilon_k-\varepsilon_f)^2+4g^2K]^{1/2}}\right)\theta(-\varepsilon^{(-)}(k)+\mu). \tag{6b}$$

We must draw attention to the fact that the total number of states in the lower band is always greater than unity because of the $(2J+1)$-fold degeneracy of the f levels. However, in view of the high densities of states of the f electrons near the upper edge of the band $\varepsilon^{(-)}(k)$, the Fermi level is separated by $\sim\rho g^2$ from the band edge. In fact, if we use the postulated constancy of the density of states in the s band and the relationship $n_s+n_f=1$, we obtain

$$\tilde{\varepsilon}_f=\frac{\rho g^2 K}{1-\rho\mu-{}^5/_6(1-n_f)^2/(1+5n_f)}.$$

We shall see later that before a transition we have $\rho\mu\sim 0.04$ and $\tilde{\varepsilon}_f\sim\rho g^2$. We find that the chemical potential lies at the very bottom of the band $\varepsilon^{(-)}(k)$, where the electron states are mainly of the f type. Therefore, the properties of SmS before the transition are those typical of a semiconductor. In the calculations of n_s ignoring the terms $(\rho g)^2$ we can assume that the Fermi level lies within the band.

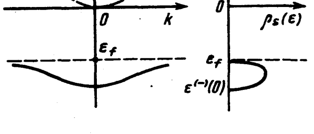

FIG. 1. Energy band scheme and density of states of the s electrons in the insulator phase. The dashed curve represents the unpertured s band and the ε_f level.

It follows from Eq. (2) that

$$n_s=6\rho\left({}^1/_2\varepsilon_f+[{}^1/_4\varepsilon_f^2+Kg^2]^{1/2}\right). \tag{7}$$

In the metal phase ($n_s\sim 1$) the chemical potential is inside the lower band and far from its bottom, as shown schematically in Fig. 2. In this case the number of the s electrons is

$$n_s=6\rho\left(\mu-\varepsilon^{(-)}(0)\right). \tag{8}$$

In general, it follows from Eqs. (3), (7), and (8) that

$$\varepsilon_f=\tilde{\varepsilon}_f\theta(\tilde{\varepsilon}_f)+\frac{1-n_f}{6\rho}-\frac{6K\rho g^2}{1-n_f}. \tag{9}$$

We shall calculate $G_f(\omega, k)$ in the metal phase using the diagram technique and the notation of Ref. 15. There is an exact relationship between G_f and G_s (Ref. 12)

$$G_f^{-1}(\omega,k)=\Sigma^{-1}(\omega_n)-g^2/(i\omega_n-\varepsilon_k). \tag{10}$$

Here, $\Sigma(\omega)$ is the self-energy part of the s function which reduces to $K_0/(i\omega_n-\varepsilon_f)$ in the zeroth approximation.

Diagrams of the first order in ρ are plotted for $\Sigma(\omega_n)$ in Fig. 3. The diagram a represents the results of renormalization of K_0. A detailed analysis shows that summation of diagrams of this type modifies K_0 to the exact average value $K=(1+2Jn_f)/(2J+1)$. Rings similar to those shown in Fig. 3b can be inserted in all the f lines and this renormalizes ε_f by $2J\rho g^2\ln(D/|\varepsilon_f|)$, which will be omitted later. As shown in Ref. 15, graphs of the c type represent a similar renormalization of K.

It follows that in the first order in ρ the form of Σ is given in the diagram d in Fig. 3 and it is described by

$$\Sigma(\omega_n)=\frac{K}{i\omega_n-\varepsilon_f}-\frac{i\pi\rho g^2(1-K^2)\operatorname{sign}\omega_n}{(i\omega_n-\varepsilon_f)^2}.$$

It should be noted that the term $g^2/(i\omega_n-\varepsilon_k)$ in the denominator G_f of Eq. (10) makes the contribution $\rho(\omega)=\pi^{-1}\operatorname{Im}G^f_{nn}(\omega)$ to the density of the f-electron states and this contribution is proportional to K^2; for the metal phase the contribution in question is of the order of $1/(2J+1)^2\sim\frac{1}{30}$ and it can be ignored. To within $(2J+1)^2$, we can assume that $G_f^{nn}(\omega)=\Sigma(\omega)$.

In the frequency range $|i\omega_n-\tilde{\varepsilon}_f|\lesssim\pi\rho g^2/K$, we shall adopt the following interpolation expression for $G_f^{nn}(\omega_n)$:

$$G_f^{nn}(\omega_n)=\frac{K}{i\omega_n-\tilde{\varepsilon}_f+i\pi(\rho g^2/K)\operatorname{sign}\omega_n}, \tag{11}$$

which is identical with Eq. (7) if $|i\omega_n-\varepsilon_f|\gg\pi\rho g^2/K$. Then, the average number of the f electrons in the metal phase at $T=0$ is

$$n_f=\frac{K}{2}\left(1-\frac{2}{\pi}\operatorname{arctg}\frac{\tilde{\varepsilon}_fK}{\pi\rho g^2}\right). \tag{12}$$

It follows from Eqs. (6) and (9) that in the case of the unperturbed level $\varepsilon_f^{(0)}$:

$$\left.\begin{aligned}\frac{\varepsilon_f^{(0)}}{6\pi\rho g^2}&=an_f-\frac{1+5n_f}{1-n_f}\frac{1}{6\pi}+\theta\left(\frac{1}{7}-n_f\right)\frac{1}{1+5n_f}\operatorname{tg}\left(\frac{\pi}{2}\frac{1-7n_f}{1+5n_f}\right),\\ a&=\frac{1}{6\pi\rho g^2}\left(2v-\frac{1}{6\rho}\right).\end{aligned}\right\} \tag{13}$$

3. We shall now consider the dependence (13) for various values of the parameter a, bearing in mind that in the case of compounds with a variable valence the number n_f is an analog of volume and $\varepsilon_f^{(0)}$ is an analog of pressure. Figure 4 shows the curves $n_f(\varepsilon_f^{(0)})$ for $a=-1, 2, 5$. An analysis of Eq. (13) shows that in the range $a\leq 0.45$ the function $n_f(\varepsilon_f^{(0)})$ is single-valued. A typical dependence $n_f(\varepsilon_f^{(0)})$ is shown for this case in Fig. 3 (curve 1). This behavior of $n_f(\varepsilon_f^{(0)})$ corresponds, for example, to the case of SmSe and SmTe (Ref. 14), i.e., to a continuous variation of the balance.

If $a>0.45$ (curves 2 and 3), the many-valued nature of $n_f(\varepsilon_f^{(0)})$ indicates the occurrence of a first-order phase transition accompanied by a change in the valence. Curve 2 in Fig. 4 describes qualitatively the transition in SmS under pressure, in the course of which n_f changes from $n_f\approx 0.75$ to 0.1. The first value of n_f is deduced from the dependence $V(p)$ before the transition[14] and the second is taken from Batlogg *et al.*[16]

We shall now consider SmS and estimate the hybridization parameter g, the position of the level ε_f relative to the bottom of the unperturbed band, and the decay constant of the f-electron level before and after the phase transition. The experimental value of the gap

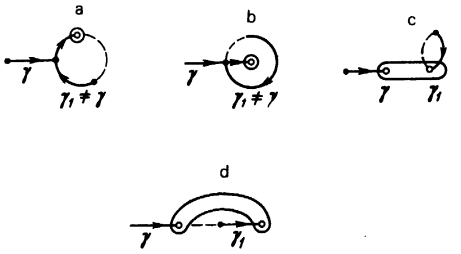

FIG. 3.

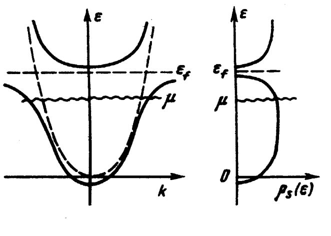

FIG. 2. Energy band scheme and the density of the s electrons in the metal phase.

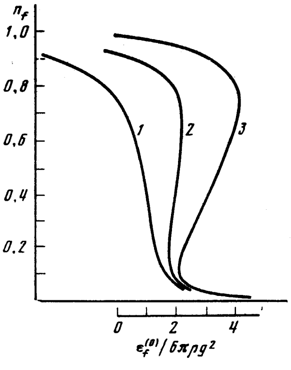

FIG. 4. Dependences of n_f on $\varepsilon_f^{(0)}$ for various values of a: 1) −1; 2) 2; 3) 5.

$\Delta=\varepsilon^{(+)}(0)-\varepsilon^{(-)}(D)$ at $p=0$ is within the range 0.065–0.15 eV (Refs. 14 and 16). We shall assume that Δ before the transition ($p\sim 6$ kbar) is $\Delta=0.07$ eV, that $n_f=0.75$, and that the characteristic value of the density of states is $\rho^{-1}=8$ eV. It follows from Eqs. (3) and (7) that

$$g=\left[\frac{1-n_f}{6\rho K}\Delta\right]^{1/2},\qquad \varepsilon_f=\frac{1-n_f}{6\rho}-\Delta. \tag{14}$$

For the selected values of Δ, n_f, and ρ^{-1}, we find that Eq. (14) yields: $g\approx 0.15$ eV; ε_f in the insulator phase before the transition ≈ 0.25 eV and after the transition $\varepsilon_f\approx 1.2$ eV. Thus, in the insulator phase the level ε_f already lies within the unperturbed conduction band and, consequently, the gap Δ is hybridized. Its width is greater than in the metal phase (in which case we have $\Delta\sim K\rho g^2\sim 10^{-3}$ eV) and this is explained by the proximity of the level ε_f to the band edge.

The decay constant of the f electrons $\Gamma=\pi\rho g^2/K$ in the metal phase ($K=\frac{1}{6}$) is of the order of 400° K for the above value of g, whereas for the semiconductor phase immediately before the transition it is $\Gamma < 50°$ K. Figure 5 shows qualitatively the structure of the s electron band before the transition, plotted for the above values of the parameters g and v.

We can thus see that correct allowance for the hybridized interaction produces a picture which is fundamentally different from that obtained in Refs. 3–6. The level ε_f lies from the beginning in the unperturbed conduction band but the system is then in the semiconductor state with a gap $\Delta\sim 0.1$–0.2 eV. On increase of pressure in the range $a<0.45$ (a depends strongly on the s–f Coulomb repulsion parameter v) the level ε_f moves upward and the lower band broadens. The number of the f electrons per site is fractional, which should be revealed experimentally first in the temperature dependence of the magnetic susceptibility, because the total momentum of the filled f shell vanishes (as in the case of Sm^{2+}). The upward movement of the level reduces the gap Δ and increases the decay constant Γ, so that the final result may be the collapse of the gap. For $\Gamma\gtrsim\Delta$, the gap becomes filled and the substance goes over continuously to the metal state. However, if the Coulomb interaction v is sufficiently strong ($a>0.45$, corresponding to $v\gtrsim 0.7$ eV for our parameters), the transition to the metal state is abrupt.

We shall conclude by noting that we have ignored the logarithmic renormalization of the f level associated with the hybridization process; it is of the order of $5\rho g^2$ for the insulator phase and $5\rho g^2\ln(D/|\tilde{\varepsilon}_f|)$ for the metal phase.[13] In the case of reasonable (from our point of view) values of the parameter $g<0.5$ eV these renormalizations can only shift the various parts of the curves in Fig. 4 by an amount smaller than unity along the abscissa but they cannot alter the transition mechanism which is due to the s–f Coulomb interaction.

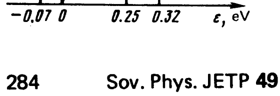

FIG. 5. Density of the states of the s electrons in SmS before a transition (schematic representation).

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APPENDIX

We shall use the spinless model, employed to describe the transition in Refs. 4–6, to show how the expression for the number of the f electrons in the insulator phase with one impurity differs from that of a regular metal. For simplicity, the term describing the Falicov repulsion will be omitted.

The Green function of the f electrons in the spinless model can be calculated exactly. In the single-impurity problem (see, for example, Ref. 17), it is of the form

$$G_f(\omega)=\left(\omega-\varepsilon_f-g^2\sum_k\frac{1}{\omega-\varepsilon_k}+i\delta\right)^{-1}$$

and gives the following expression for n_f in the insulator phase:

$$n_f=\left(1+g^2\sum_k\frac{1}{(\tilde{\varepsilon}_f-\varepsilon_k)^2}\right)^{-1},\qquad \tilde{\varepsilon}_f=\varepsilon_f+g^2\sum_k\frac{1}{\tilde{\varepsilon}_f-\varepsilon_k}. \tag{A.1}$$

The expression (A.1) is identical with n_f from Eq. (6a) (we must bear in mind that in the spinless case we have $K=1$) only in the limit $g/\Delta\ll 1$. It follows from the main text above that before a transition we have $g/\Delta\sim 2$, i.e., the single-impurity treatment then becomes invalid.

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