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Valence transitions in rare-earth chalcogenides

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The equation of state for samarium chalcogenides is calculated at $T = 0$ in a model in which the promotion of an electron from f level to d band is accompanied by a lattice contraction so that the chemical potential of the d electrons is reduced. With the nonlinearity in the lattice contraction as a function of d band occupation taken as a variable parameter and using known spectroscopic and elastic data on samarium chalcogenides, an equation of state is calculated which agrees to within 20% with the experimental results.

I. INTRODUCTION

Owing to the increasing importance of Hund's-rule couplings as we approach the middle of the rare-earth series, Sm and Eu occur as 2^+ ions in most of their compounds, whereas the other rare-earth elements occur as 3^+. The final occupied f level is, however, not far below the d level. In compounds the d levels broaden into a band hybridizing in the process with the $6s$ levels but the f levels are relatively less affected. Under pressure the lower of the crystal-field d bands move down (and broaden) and may cross the f level. Near the pressure where this crossing occurs a rapid continuous (in SmTe and SmSe) or discontinuous (in SmS) change in the P-V relation has been observed as also a change in the resistivity.[1] Additional information has been obtained through x-ray-photo-emission-spectroscopy (XPS) measurements.[2] The phenomenon has obviously to do with the transfer of some of the f electrons to the much wider s-d bands and the large difference in the f^5 and the f^6 ionic volume.

We investigate here the extent to which just this large difference in ionic volume is responsible for the observed behavior of the equation of state. A model is considered in which the transfer of an electron from f to d is accompanied by a lattice contraction so that the chemical potential of the d electrons is lowered. With a parabolic conduction band (in the absence of Coulomb interactions) the lattice is always stable for small valence change. Its stability for further valence change depends on the extent to which the lattice contraction depends nonlinearly on the valence change. By treating the nonlinearity as a variable parameter and using the available experimental data for the other parameters, we can calculate an equation of state which agrees to within 20% with the experimental results in SmTe, SmSe, and SmS.

This agreement however does not solve the problem of the rare-earth chalcogenides since we neglect all effects arising from Coulomb correlations. In the usual picture of a metal-insulator transition, these correlations play an essential role and the transition is generally first order in nature due to the long-range nature of the Coulomb interaction. A question which we leave unanswered is the relative role of Coulomb effects and nonlinear lattice effects. Nor do we give any justification of the variation of the nonlinearity parameter in going from the sulfide to the telluride compounds. Another important question in many rare-earth chalcogenides is the observed absence of magnetic moments in the "metallic" phase.[3] This problem has recently been attempted by Varma, Yafet and Cohen.[4] A qualitative discussion of these points has recently been given by Mott.[5]

The paper is organized as follows. In Sec. II, we generate a mean-field Hamiltonian to illustrate microscopically the physics of the expression we write down in Sec. III for the energy as a function of valence and volume. In Sec. IV we calculate the equation of states and obtain numerical results and comment on our results.

II. MICROSCOPIC THEORY

The electronic part of the Hamiltonian in our problem describes atomic f levels that hybridize with the d levels on neighboring atoms and a d band separated by a gap from the f levels:

$$H_e = \sum_i E_f n_{fi} + \sum_{k\sigma} (E_0 + \epsilon_k) n_{k\sigma} + \sum_{k\sigma i} V_{kf} \times (C^\dagger_{k\sigma} C_{fi} + \text{c. c.}). \tag{1}$$

The f-d gap described by H_e is $E_0 - E_f$. For simplicity we take the lattice Hamiltonian to be that of Einstein oscillators at each site,

$$H_l = \omega_0 \sum_i b_i^\dagger \, b_i . \tag{2}$$

The interaction Hamiltonian is written down from the following considerations: The ionic volume in the $f^{n-1}d$ configuration is less than that in the f^n configuration. Around the $f^{n-1}d$ configuration, the lattice distorts (assuming slow fluctuation from one to the other configuration; see discussion at the end) leading to a depression in the local d level and an effective reduction in the f-d gap. Since the zero of the energy is chosen arbitrarily, we can express the coupling to the lattice in the form involving the number of f electrons per site. Restricting ourselves for simplicity to the case where only f^0d and f^1 configurations are involved,

$$H_{\text{int}} = \sum_i \lambda(1-n_{fi})(b_i + b_i^\dagger)\,. \tag{3}$$

In this form we obtain compression of the lattice for $n_{fi} \neq 1$. Next, we approximate H_{int} in a mean-field fashion,

$$H_{\text{int}}^{\text{MF}} = \lambda \sum_i [\,(1-n_{fi})\langle b_i + b_i^\dagger\rangle + (1-\langle n_{fi}\rangle)(b_i + b_i^\dagger) - (1-\langle n_{fi}\rangle)\langle b_i + b_i^\dagger\rangle\,]\,. \tag{4}$$

We can express $\langle b_i + b_i^\dagger\rangle$ in terms of $\langle n_{fi}\rangle$ by noting that the ground state of $H_l + H_{\text{int}}$ is related to the ground state of H_l by the displaced oscillator transformation,

$$|0'\rangle = \exp\left(\frac{\lambda\langle 1-n_f\rangle}{\hbar\omega_0}\right)(b+b^\dagger)\quad|0\rangle\,, \tag{5}$$

so that

$$\langle 0'|\,b+b^\dagger\,|0'\rangle = -\,2\lambda\langle 1-n_f\rangle/\omega_0\,. \tag{6}$$

Using (4) and (6) in (1) and (2), the mean-field electronic Hamiltonian is

$$H_e^{\text{MF}} = \sum_i \left(E_f + \frac{2\lambda^2}{\omega_0}\langle 1-n_f\rangle\right) n_{fi} + \sum_{k\sigma}(E_0+\epsilon_k)\,n_{k\sigma} + \sum_{k\sigma i} V_{kf}(C_{k\sigma}^\dagger C_{fi} + \text{c. c.})\,, \tag{7}$$

and the mean-field lattice Hamiltonian is

$$H_l^{\text{MF}} = \sum_i \omega_0 b_i'^\dagger b_i' - (1-\langle n_f\rangle)\left(\frac{\lambda^2}{\omega_0} - \frac{2\lambda}{\omega_0}\langle 1-n_f\rangle\right), \tag{8}$$

where

$$b_i' = b_i + \lambda(1-\langle n_f\rangle)/\omega_0\,. \tag{9}$$

We see from (7) that the gap between the f level and the d band is reduced by transfer of electrons out of the f level:

$$E_{\text{gap}} = E_0 - \left(E_f + \frac{2\lambda^2}{\omega_0}\langle 1-n_f\rangle\right)\,. \tag{10}$$

In the above mean treatment, we have not considered the effect of H_{int} on the f-d mixing term. This has recently been considered by Sherrington and van Molnar.[6] The result is to give a reduced V_{kf} due to phonon overlap factors. The reduction increases with temperature just as in the similar problem of small polaron hopping.

Within mean-field theory the problem is solved from Eq. (7) by determining $\langle n_f\rangle$ self-consistently. The hybridizing term may be handled by introducing the Green's function

$$G_{ff}(\omega) = \frac{1}{\omega - E - \Sigma(\omega)}\,, \tag{11}$$

where

$$\Sigma(\omega) = \sum_k |V_{fk}|^2 \frac{1}{\omega - \tilde{\epsilon}_k - i\delta}\,, \tag{12}$$

where

$$\tilde{\epsilon}_k = E_f + 2\lambda^2\langle 1-n_f\rangle/\omega_0 + \epsilon_k\,. \tag{13}$$

The f-electron density of states is given by

$$\rho_f(\omega) = (1/\pi)\,\text{Im}\,G_{ff}(\omega)\,. \tag{14}$$

The character of Σ is radically different when the "self-consistent" f level is below or above the bottom of the band. In the former case Σ is real and in the latter it is complex.

The f-state occupation at an energy

$$\mathcal{E}_f = E + \Sigma(\mathcal{E}_f) \tag{15}$$

is

$$n(\mathcal{E}_f) = \lim_{\epsilon\to 0}\frac{1}{\pi}\int_{\mathcal{E}_f-\epsilon}^{\mathcal{E}_f+\epsilon} \text{Im}\,G_{ff}(\omega)\,d\omega\,, \tag{16}$$

which can be evaluated to be

$$n(\omega) = \left|\left(1 - \frac{d\Sigma}{d\omega}\right)^{-1}\right| = \left|\left(1 + \sum_k \frac{|V_{fk}|^2}{(\omega-\epsilon_k)^2}\right)^{-1}\right|\,. \tag{17}$$

Thus already with the f level below the band, the f-state occupation is $n(\omega)$ rather than 1 due to the hybridization effects.

If V in (17) has a slower than $k^{1/2}$ dependence, the sum in the denominator diverges as the band edge is approached ($\omega \to 0$). This fact has been recently exploited by Anderson and Haldane[7] for the problem of transition-metal impurities in semiconductors. In our case if we take the conduction band to be s-like at the edge $V_{fk} \sim k^3$ and effects arising from (17) seem unimportant. We have not investigated (17) for the case of the actual band structure in rare-earth chalcogenides.

III. MEAN-FIELD CALCULATIONS

The above theory is only meant to be illustrative of a few simple points—that the strongly phonon-coupled valence-change problem has the features of nonlinearity (and hybridization) which can give rise to phase transitions. Detailed quantitative results cannot be expected from such a theory because it neglects several important effects. For example the volume change in the model is only linearly related to the change in valence. Clearly interactions between ions of different sizes will lead to nonlinear relation between valence and volume. The phonons are taken to be purely local and the volume dependence of various parameters is not taken into account.

In mean-field theory some of these defects can be remedied by writing down a free energy which is a function of the average number of conduction electrons per atom Z, and the volume per atom V. Thus Z corresponds to $1-\langle n_f\rangle$ of the microscopic theory. At $T=0$

$$E(Z,V)=E_l+E_e\,, \tag{18}$$

where E_l is the lattice contribution and E_e, the electronic. We write

$$E_l=B(V)(V-V_0)^2/2V_0\,, \tag{19}$$

where $B(V)$ is the (volume-dependent) bulk modulus and V_0 is the equilibrium volume for a given Z from lattice considerations alone:

$$V_0=V_2Z+(1-Z)V_3-V_4Z(1-Z), \tag{20}$$

where V_2 and V_3 are the volumes for the solid composed of 2^+ and 3^+ ions, respectively (with samarium chalcogenides in mind), and we have introduced a nonlinearity parameter V_4. We have defined V_0 such that it is the equilibrium volume if E_l were the only contribution to the energy. The actual equilibrium volume is of course determined from minimization of (18). Equation (20) represents the nonlinear generalization of Eq. (9).

We also include the volume dependence of the bulk modulus as given by the empirically observed relationship[8]

$$B(V')=B(V)(V/V')^{\gamma}\,, \tag{21}$$

with $\gamma\simeq 1.3$.

The electronic energy is given by

$$E_e=Z(E_g\Theta(E_g)+E_B)\,, \tag{22}$$

where E_g is the distance from the f level to the bottom of the s-d band, E_B is the band energy, and $\Theta(E_g)=1$ for $E_g>0$, i.e., bottom of conduction band above the f level, and $\Theta(E_g)=0$ for $E_g<0$. Experimentally the linear variation of E_g with pressure (or volume) is known through spectroscopic data. The variation of E_g with volume comes about mostly due to the change in the conduction bandwidth and the movement of the center of the conduction band with volume. The variation of the d-electron bandwidth $W(V)$ is taken to be[9]

$$W(V)=W(V')(V/V')^{-5/3}\,. \tag{23}$$

We assume that the decrease of E_g with decreasing volume is given by a similar function,

$$E_g(V)=E_g(V')\left(1+\beta\frac{V-V'}{V'}\right)^{-5/3}\,, \tag{24}$$

and adjust the coefficient β by comparing the linear term with the experimentally observed results. We assume the band to be parabolic so that we get

$$ZE_B=\tfrac{3}{5}(3/\pi)^{2/3}\,W(V)\,Z^{5/3}\,, \tag{25}$$

where we have considered a nondegenerate submultiplet of the s-d band. The electronic energy is of course calculated with the requirement that in the "metallic" phase the chemical potential of the f electrons coincides with the Fermi level of the conduction electrons. The energy functional (18) includes in mean-field theory all the effects discussed in the earlier theoretical treatment, Sec. III, except one (of course it has several additional features). The one that it does not include is the effect of hybridization. We saw that hybridization leads to an effective renormalization of the f-state occupation to less than 1 according to (17). If we take $V_{fk}\sim k^3$, this is unimportant. Even in this case, however, hybridization may be important for understanding the magnetic properties.

IV. EQUATION OF STATE

The total energy is a function of two variables, the fractional valence Z and the volume V. At equilibrium we must have

$$\frac{\partial E}{\partial Z}=0 \quad \text{for} \quad Z>0\,. \tag{26}$$

This provides us with a relationship $Z(V)$ at equilibrium. For the equilibrium position to be stable, the determinant of the second derivatives of E with respect to Z and V must be positive. This condition can be easily shown to be equivalent to the condition that $dP/dV<0$. We have at equilibrium

$$-\frac{dP}{dV}=\frac{\partial^2E}{\partial V^2}-\frac{(\partial^2E/\partial Z\partial V)^2}{\partial^2E/\partial Z^2}>0 \tag{27}$$

for stability. Inserting $Z(V)$ obtained from (26) into (27) and integrating, the equation of state, P vs V, can be calculated. A similar procedure to obtain a $P(V)$ relation has been used by Hirst[10] but not on the basis of the same physics.

These calculations were done numerically using the parameters given in Table I. The d bandwidth at atmospheric pressure was taken to be 2.5 eV. consistent with the band-structure calculation by Davis.[11] Apart from this we really have only one undetermined parameter, V_4 for each material. The P-V curves for parameters suitable for SmS, SmSe, and SmTe are shown in Figs. 1(a)–1(c). For SmSe and SmTe, the experimental results fall within ± 10% of Figs. 1(a) and 1(b). For SmS, we have adjusted V_4 to get the correct pressure for the discontinuous transition. We then get a volume discontinuity of 12% to be compared with the experimental discontinuity of about 10%. We have not plotted the experimental results[1] in Fig. 1, since the theoretical curves essentially fall on them. This agreement is not as spectacular as one might think. After all, the initial slope and the slope after the transition region is more or less fixed by the empirical relation given by Eq. (21). We are merely fitting the transition region, which can easily be fitted by a two-parameter curve. We choose one of them for each material and seem to get the other one correctly from the theory.

The nonlinearity parameter V_4 is quite large. We note that in going from SmTe to SmS the required variation in V_4 is in the same *direction* as suggested by Anderson and Chui.[12] However the sign of V_4 in each case is attractive from the point of view of the transition under pressure.

In the curves we have also drawn the equilibrium fractional valence we have obtained at each pressure. It is noteworthy that even in SmS, we find a finite value of Z before the transition. This is due to the $Z^{+5/3}$ contribution of the banding energy. The value of Z slowly increases with increasing pressure above the transition. The fact that valence changes fractionally has to do with the assumed large (δ function in the) density of states for the f levels. On the scale of the conduction bandwidth this is all right. On the other hand, we believe that neglect of hybridization is probably only valid at temperatures of the order of or larger than the hybridization energy, which may be of the order of a few hundred degrees. Owing to the coherent motion of the f hole due to hybridization the effects arising from volume difference between the f^6 and f^5 configurations are likely to be reduced. This is an amusing point and worth discussing a little.

If $V_a(R)$ and $V_b(R)$ are the potential energies for the two valences, as a function of the nearest neighbor distance, the average nearest-neighbor distance is different if valence fluctuation is at a rate much faster or much slower than the inverse of the characteristic phonon frequency. First take the case that the valence fluctuation is at a very slow rate. Then the nearest-neighbor distance around valence a, R_a, is given by

$$\frac{dV_a}{dR}=0$$

and that around valence b, R_b, is given by

$$\frac{dV_b}{dR}=0,$$

so that the average nearest-neighbor distance is

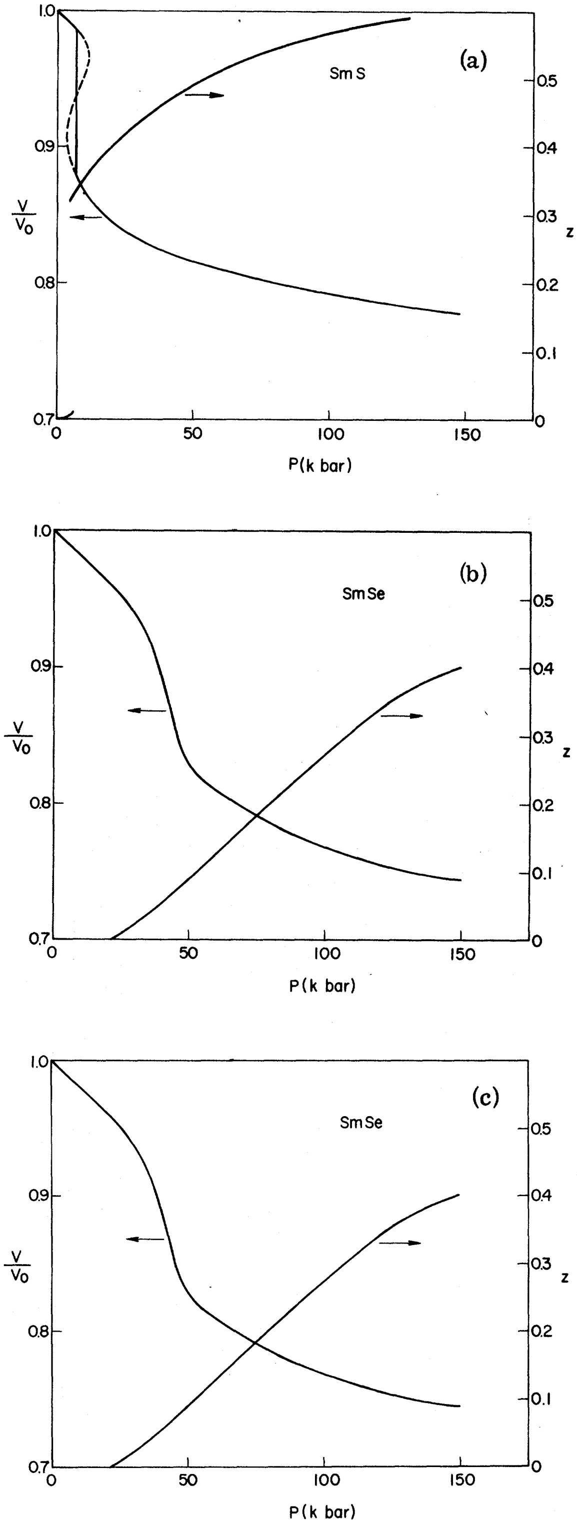

FIG. 1. (a) Pressure vs volume and valence vs volume calculated for SmS using parameters given in Table I. An equal-area construction has been used to find the discontinuity in volume. (b) Pressure vs volume and valence vs volume calculated for SmSe. (c) Pressure vs volume and valence vs volume calculated for SmTe.

TABLE I. Parameters used to calculate the equations of state shown in Fig. 1. $W(P=0)$ is taken from Ref. 6. V_4/V_2 is an adjustable parameter. The other parameters have been collected in Ref. 7.

	B (kbar)	$E_g(P=0)$	$\partial E_g/\partial P$ (MeV/kbar)	$\frac{V_2-V_3}{V_2}$	$\frac{V_4}{V_2}$	$W(P=0)$ (eV)	γ
SmS	476	0.1	−11.9	0.17	−1.1	2.5	1.3
SmSe	520	0.5	−11.0	0.17	−0.6	2.5	1.3
SmTe	400	0.7	−10.0	0.16	−0.5	2.5	1.3

$$R_{\text{av}}^{\text{slow}} = n_a R_a + n_b R_b ,$$

where n_a is the fraction of atoms in valence a and n_b that in valence b. If, however, the fluctuation rate is very fast compared to the inverse phonon frequency, the nearest-neighbor distance $R_{\text{av}}^{\text{fast}}$ is uniform throughout the system and is given by

$$\frac{d}{dR}\left[n_a V_a(R) + n_b V_b(R)\right] = 0.$$

$R_{\text{av}}^{\text{slow}}$ snd $R_{\text{av}}^{\text{fast}}$ will be different if the system is anharmonic. Usually $V_{a,b}(R)$ departs from harmonicity by being less rapidly varying above $R_{a,b}$ than below $R_{a,b}$. From this we can immediately conclude that $R_{\text{av}}^{\text{fast}}$ is larger than $R_{\text{av}}^{\text{slow}}$.

Finally, we make a comment on the role of Coulomb interactions neglected throughout the paper. Brinkman and Rice[13] have argued that the Coulomb interactions manifest themselves most importantly in the exciton-exciton interaction, which leads to a quadratic term[14] in the expansion of the free-energy in powers of the density of carriers at low densities. Generally this interaction is attractive and large enough to lead to first-order insulator-to-metal transitions. (This argument is valid under the assumption that the low-density expansion is well behaved.) Applied to our case, it would have to mean that our nonlinearity coefficients V_4 are phenomenological and include perhaps both the effect of the nonlinear response of the lattice and the Coulomb effects. A microscopic separation of the two contributions is a very difficult task.

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