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A NOTE ON THE EQUATION OF STATE FOR SYSTEMS THAT UNDERGO VALENCE CHANGES[*]

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By considering the effects of valence changes on the parameters that determine the cohesive energy of samarium monochalcogenides, we discuss the equation of state for these systems and provide a basis for the understanding of the anomalous pressure dependence of the compressibility that is found experimentally.

1. INTRODUCTION

THERE has been great interest recently in rare-earth compounds that undergo pressure-induced phase changes, caused by the delocalization of a $4f$ electron.[1–7] The transition is associated with a change in the electrical conductivity of the compounds, since the electron goes from a localized $4f$ state to the extended $5d$ band.[1,2,5]

Typical examples of this type of system are the samarium monochalcogenides[1–5] (SmS, SmSe, SmTe). These compounds crystallize in the NaCl structure, which is not changed at the transition.[4] SmS has a first-order transformation at 6.5 kbar, whereas SmSe and SmTe undergo a slow transformation in the range 10–60 kbar. As pointed out by Jayaraman *et al.*,[1] the transition is caused by the shrinkage of the energy gap between the $4f$ level and the conduction band as pressure is applied. On the basis of the Falicov–Kimball[8] model of metal–insulator transitions, in which the Coulomb interaction between $4f$ and $5d$ electrons plays an essential role, Bucher and Maines[5] has discussed the occurrence of first-order and slow transitions.

From the microscopic point of view it is more convenient to take the volume as the fundamental variable, and calculate the parameters of the system as functions of interatomic separation. On the other hand, the experiments are performed using pressure as the independent parameter, so that one is led to consider the equation of state for these systems.

In this paper we want to discuss in a simple way the equation of state of a system that undergoes valence changes. This requires consideration of the cohesive energy of the compounds which is, in general, a major problem. For this reason we shall consider only those compounds which are mainly ionic in character, so that their cohesive energy can be reasonably described by the Madelung and repulsive core contributions.[9] In fact, the collapsed phases form rather poor metals and there should still be a high degree of ionicity left, as is indicated by the stability of the NaCl structure.

2. THE MODEL

At zero temperature, the internal energy of such a system can be written as

$$\mathcal{E} = \mathcal{E}_0(V) + \mathcal{E}_e,$$

where $\mathcal{E}_0(V)$ is the ionic contribution and $\mathcal{E}_e$ is the electronic part. In order to describe the most important effects of the valence changes in the equation of state,

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we take[9] $\mathcal{E}_0(V) = z\lambda \exp(-R/\rho) - Mq^2/R$, where λ is the strength of the repulsive force, z is the coordination number ($z = 6$ for NaCl structure), R is the nearest neighbour separation, ρ is the characteristic distance for the repulsive interaction, $M = 1.75$ is Madelung's constant, and q is the ionic charge. It should be noted that a more careful evaluation of the cohesive energy would require other contributions to be taken into account (covalency in the insulating phase and electron gas effects in the metallic phase). From a phenomenological point of view, however, one expects that the simple form (1) would be sufficient to account for the volume dependence of the crystal energy.

If we call $n (0 \leqslant n \leqslant 1)$ the number of holes in the f shell, and assume a constant density of states for the conduction band,[8] the electronic contribution to the energy can be written $\mathcal{E}_e = \sum_k \epsilon_k n_k + \Delta n - Gn \sum_k n_k$, where ϵ_k are the one-particle energies in the conduction band, n_k is the occupation of the band states ($n_k = 1$ for $k < k_F$ and $n_k = 0$ for $k > k_F$). Δ is the energy necessary to create a hole in the f shell of the Sm^{++}ion and G is the Coulomb attraction between localized holes and conduction electrons.[8] Assuming a square density of states and taking into account $n = \sum_k n_k$ (charge conservation) the electronic energy can be written in the form[10] $\mathcal{E}_e = En + Bn^2$, where E is essentially the distance from the $4f$ level to the bottom of the conduction band; B has a positive contribution due to the filling of the conduction band and a negative contribution due to electron–hole attraction. A different choice for the density of states or a more sophisticated treatment of the electron–hole interaction[5,11] will, in general, lead to a more complicated dependence of $\mathcal{E}_e$ on n, but the form given above is the simplest that can give rise to either first-order or second-order transitions. Indeed, for $B > 0$ one finds the least value of $\mathcal{E}_e$ at $n = 0$ for $E > 0$, at $n = -E/2B$ for $-2B < E < 0$ and, at $n = 1$ for $E < B$, whereas for $B < 0$ there is an abrupt change in the value of n for which $\mathcal{E}_e$ has a minimum.

For $n = 0$, the equilibrium separation at zero pressure R_0 is determined by $(\mathrm{d}\mathcal{E}/\mathrm{d}R) = 0$ which implies $R_0^3 \exp(-R_0/\rho_0) = (Mq^2\rho_0)/z\lambda$. Clearly the hard core radius ρ is determined by the occupancy of the $4f$ shell. Since the $4f$ electron delocalization implies a change in this occupancy, ρ will change at the transition in a way which can be accounted for by taking $\rho = \rho_0 (1 - \alpha n)$. For the rare-earth monochalcogenides, one can infer from the lattice constant changes[12] that $\alpha \sim 0.06$. To discuss the volume–pressure relation in the general case, we take for the equilibrium separation $R = R_0(1 - \Delta)$, where Δ will generally include the effect of pressure and of changes in n. Strictly speaking, the change in n will certainly be accompanied by changes in λ as well, which we neglect.

The electronic terms E and B will change with interionic separation; for not too large changes in R we can take

$$E = E_0 - \gamma R_0 \Delta$$

and assume that B does not change. From a recent calculation for SmS by Herbst *et al.*[13] one can estimate by a linear interpolation, that γ lies somewhere between 2 and 35 eV/Å. At finite pressure we must consider the enthalpy per Sm ion $\mathcal{H} = \mathcal{E} + pV = \mathcal{E} + 2pR^3$ and determine the volume pressure relation through

$$\frac{\partial \mathcal{H}}{\partial V} = 0.$$

In view of the qualitative nature of the assumption we have made, it is not worth considering the full volume dependence of $\mathcal{H}$. We shall instead expand $\mathcal{H}$ to second order in n and Δ, which suffices for our purposes. In this way we obtain $\mathcal{H} = a + b\Delta + c\Delta^2$, where

$$a = \frac{Mq^2}{R_0}\left(\frac{\rho_0}{R_0} - 1\right) + 2pR_0^3 + \tilde{E}n + \tilde{B}n^2$$

$$b = -6pR_0^3 - 6p_0R_0^3 n$$

$$c = 6pR_0^3 + 3p_1R_0^3$$

with

$$p_0 = \frac{1}{6R_0^3}\left[\gamma R_0 + Mq^2\alpha\left(\frac{1}{\rho_0} - \frac{1}{R_0}\right)\right]$$

$$p_1 = \frac{Mq^2}{6R_0^3}\left(\frac{1}{\rho_0} - \frac{2}{R_0}\right)$$

$$\tilde{E} = E_0 - \frac{Mq^2}{R_0}\alpha, \quad \tilde{B} = B + 3R_0^3 p_1 \alpha^2.$$

Note that p_1 is three times the bulk modulus.[9] These relations imply $\Delta = (p_0 n + p)/(p_1 + 2p)$. Since p_1 is of

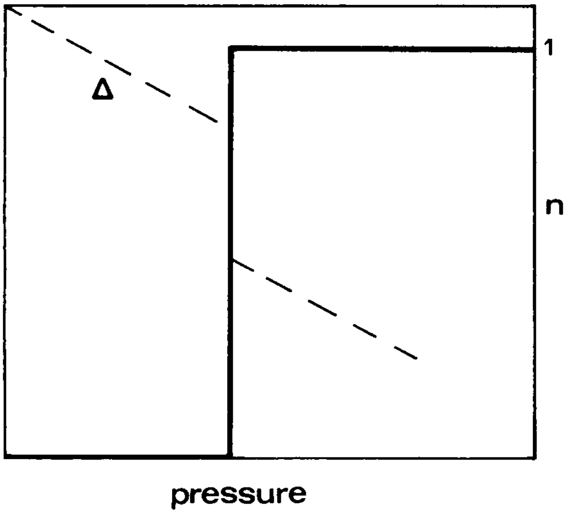

FIG. 1. Number of holes n in the f level (full line) and lattice constant change Δ (dotted line) as functions of pressure for a first-order transition.

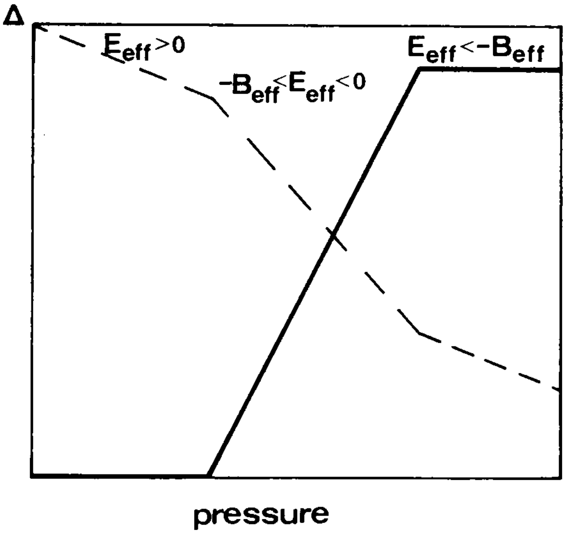

FIG. 2. Number of holes n in the f level (full line) and lattice constant change Δ (dotted line) as functions of pressure for a slow transition.

the order of 1500 kbar, one can drop p in the denominator; in this case the relation gives the explicit variation of Δ with pressure, with a coefficient related to the bulk modulus, plus the dependence induced through changes in n. Using the experimental values for R_0 we estimate $\rho_0 \sim 0.46$ Å and $p_0 \sim 200$ kbar. From this we find γ of the order of 4 eV/Å.

Inserting Δ back into $\mathcal{H}$ we can finally obtain

$$\mathcal{H} = \mathcal{H}_0 + E_{\text{eff}} n + B_{\text{eff}} n^2,$$

where $\mathcal{H}_0$ is independent of n and

$$\begin{aligned} E_{\text{eff}} &= \tilde{E} - 6R_0^3 \frac{p_0 p}{p_1 + 2p} \\ &\cong \tilde{E} - 6R_0^3 \left(\frac{p_0}{p_1}\right) p. \\ B_{\text{eff}} &= \tilde{B} - 3R_0^3 \frac{p_0^2}{p_1 + 2p} \\ &\cong \tilde{B} - 3R_0^3 \frac{p_0^2}{p_1}. \end{aligned}$$

We see from here that our description involving a deformable lattice implies that the electronic energy term E_0 is replaced at zero pressure by $\tilde{E}$, which accounts for the change in the crystal energy due to the shrinking of the lattice. Our expression for E_{eff} contains a pressure dependence; we see that, within the approximation we are working, one recovers the linear dependence on p used in the work of Ramirez and Falicov.[14]

For similar reasons, the change in cohesive energy modifies the value of B obtained from electronic considerations only. To the same degree of accuracy, B_{eff} is independent of pressure, as indicated above. For $B_{\text{eff}} > 0$, the equilibrium value for n will be either 0 or 1 according to whether $E_{\text{eff}} + B_{\text{eff}}$ is positive or negative. Since E_{eff} decreases with pressure, there will be an abrupt transition when $E_{\text{eff}} + B_{\text{eff}} = 0$. This relation gives for the critical pressure:

$$p_c = \frac{\tilde{E} + \tilde{B}}{6R_0^3 p_0} p_1 - \frac{p_0}{2}.$$

For $B_{\text{eff}} > 0$ the equilibrium value of n depends on the value of E_{eff}. If $E_{\text{eff}} > 0$, $n = 0$. If $E_{\text{eff}} < 0$ but greater than $-B_{\text{eff}}$, then

$$n = -\frac{E_{\text{eff}}}{2B_{\text{eff}}} = -\frac{\tilde{E} - 6R_0^3 \dfrac{p_0}{p_1} p}{2\tilde{B} - 6R_0^3 \dfrac{p_0^2}{p_1}}.$$

For E_{eff} smaller than $-B_{\text{eff}}$ the solution is $n = 1$. The corresponding value of n for each case must be

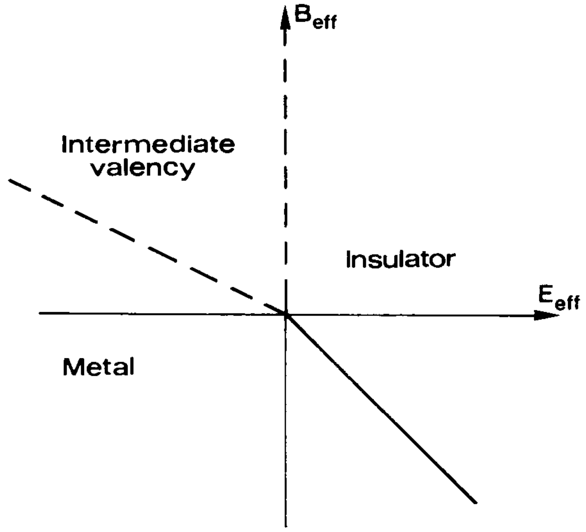

FIG. 3. Phase diagram of system undergoing valence changes in the E, B plane.

substituted into Δ to get the pressure dependence of Δ and the corresponding volume–pressure relationship (equation of state at zero temperature).

Figure 1 shows the qualitative behaviour of n and of the relative lattice constant change Δ as functions of pressure, for $B_{eff} < 0$, i.e. when a first-order transition takes place. Figure 2 is the equivalent graph for $B_{eff} > 0$, corresponding to a slow transformation. Among the rare-earth monochalcogenides that have been studied experimentally,[1–5] SmS corresponds to the first case, whereas SmSe, SmTe, TmTe and YbTe are examples of the second class. This interpretation of the first- and second-order transitions is similar to that given by Bucher and Maines.[5] Figure 3 gives the phase diagram for out simplified model in the (E_{eff}, B_{eff}) plane.

3. DISCUSSION

It is obvious that this treatment of the equation of state can give only a qualitative description of the rare-earth compounds that undergo pressure-induced valence changes. Some of the ideas we have elaborated here were already implicit in the earlier work of Falicov *et al.* and of Bucher and Maines. In order to get more quantitative agreement one should include several effects:

(i) $4f$–$5d$ hybridization. This would yield a rounding-off of the curves depicted in Figs 1 and 2. A similar effect has been found in the case of Ce by Alascio *et al.*[15]

(ii) Finite temperature effects. To consider these effects one should include the lattice and electron entropies; the latter along the lines indicated in references 8 and 14. In the case of Sm, since the higher spin–orbit multiplets lie quite close to the ground state, one would be led to consider effective temperature dependent multiplicities,[10] even neglecting crystal field effects. As in the case of hybridization, finite temperature must lead to a rounding-off of the curves of Figs. 1 and 2.

(iii) We have considered here a mean field theory in the sense that the changes in R and ρ are taken to be uniform throughout the crystal. Should it prove necessary, the theory might be refined to incorporate the effect of local changes in ρ.

(iv) The crystal has been assumed to have the same degree of ionicity in both insulating and metallic phases. Since the band states are thought to be derived primarily from the Sm $5d$ states,[1] this should not be a serious shortcoming in the model. If one were to effectively evaluate the cohesive energy, it would be necessary to take into account the fact that electrons in the metallic phase will tend to partially screen the ionic interactions.

It is thought that in some transition metal ionic compounds the transition occurs through the promotion of a hole from a transition metal $3d$ band to a cation p band.[8] In this case there is a charge transfer between the components of the ionic crystal taking place together with the transition. This effect can be included in the above discussed scheme by allowing q to vary with n.

Since the change in interionic Coulomb interaction (corresponding to a change in R when n goes from zero to one) is of the order of 1 eV, we feel that the cohesive energy should not be left out in the calculation of the parameters, relevant to the transition. It is also worth mentioning that the effective pressure dependence of E_{eff} given by (13a) – apart from the contribution due to the assumed volume dependence of E – contains, through p_0/p_1, a contribution from the cohesive terms which is of the same order of magnitude as the experimentally determined pressure dependence.

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L'équation d'état des monochalcogenides de samarium est étudié, prenant en consideration les effets de charge de valence sur les paramètres qui déterminent l'énergie de cohesion. L'explanation pour la dépendence anomalique de la compressibilité experimentale sur la pression est aussi donnée.