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PHASE DIAGRAM OF SAMARIUM MONOCHALCOGENIDES

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By using a simple ionic model for the cohesive energy and electronic terms similar to those of the Falicov–Kimball model for metal–insulator transitions we obtain a phase diagram for SmS with a critical point at $Tk = 554°K$. The model reduces to the thermodynamic theory proposed by Aptekar and Ponyatovskiy and allows to calculate the $p-V$ isotherms for SmS, SmSe and SmTe, and the concentration of holes in the $4f$ shell as functions of pressure and temperature.

WE REPORT here the results of a calculation of the equation of state for the Sm monochalcogenides which are known to undergo valence changes under pressure of alloying.

There exists a wealth of experimental information on these systems, which although not establishing unique values for some of the parameters, clearly point out the nature of the transition. Resistivity,[1,2] and heat capacity,[3] magnetic susceptibility[4–8] and crystal structure[9] have been studied in the insulating low pressure phase and in the metallic high pressure phase. Optical properties[10,11] have also been determined.

These compounds crystallize in the ClNa structure, and at zero pressure are semiconducting with the Sm ions being divalent. There is clear indication that in this phase conductivity is due to thermal activation of electrons from very localized $4f$ Sm levels into a broader $5d$ band. The energy gaps have been established to be 0.20, 0.46 and 0.63 eV for SmS, SmSe, SmTe respectively. Under pressure all three compounds go into a metallic state,[4] without change in crystal structure.[9] The transition is abrupt for SmS and slow for SmSe and SmTe, and is accompanied by a volume contraction[9] of about 20 per cent.

In this letter we discuss the equation of state for these systems, and determine the phase diagram and the pressure–volume isotherms. Since the systems we have in mind are mainly ionic in character, their cohesive energy can be reasonable described by the Madelung and repulsive core contributions.[12] The collapsed phases form poor metals and the stability of the NaCl structure indicates that there is a high degree of ionicity left in the metallic state. The relevant part of the internal energy is then:

$$\mathcal{E} = \mathcal{E}_B + \mathcal{E}_L \qquad (1)$$

$\mathcal{E}_B$ is the electronic energy which we approximate[12–14] by

$$\mathcal{E}_B = En + Bn^2 \,. \qquad (2)$$

E is the energy which would be necessary to create a hole in the $4f$ shell in a rigid lattice. B has a positive constribution due to the filling of the $5d$ band and a negative contribution due to electron–hole attraction. This form of the electronic energy results from a rigid band calculation for a square density of conduction states.[15]

The cohesive energy is $\mathcal{E}_L = 6\lambda\, e^{-R/\rho} - (Mq^2/R)$, where λ is the strength of the repulsive force, R the

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Table 1. Parameters used in this calculation

Substance	R_0(Å)	E(eV)	B_{eff}(eV)	p_0(kbar)	Γ(eV/kbar)
SmS	2.987	0.2	−0.095	151	0.0126
SmSe	3.112	0.46	0.10	157	0.0148
SmTe	3.298	0.63	0.20	106	0.0119

nearest neighbor separation, ρ the characteristic distance for the repulsive interaction, M is the Madelung constant and q the ionic charge.

To write the entropy we neglect the contributions of the conduction band and the lattice. The entropy associated with the holes can be written as a sum of two terms:[13,14] (i) Configuration disorder: $S_{conf} = -K\{n \ln n + (1-n)\ln(1-n)\}$; (ii) Spin disorder entropy: $S_s = k\{n \ln Q_M + (1-n)\ln Q_I\}$. Where Q_M and Q_I are the spin multiplicities of the metallic and insulating phase.

Since the splitting between the ground state $^7F_0$ and the first excited configuration $^7F_1$ of the divalent Sm ion is 410°K,[6] and in the trivalent state the crystal field splits the $J = 5/2$ sextuplet into a doublet (Γ_7) and a quadruplet (Γ_8) which lie according to Bader *et al.*[3] some 165°K apart, we must take temperature dependent values for Q_M and Q_I, $Q_M = 2 + 4e^{-165/T}$; $Q_I = 1 + 3e^{-410/T}$.

The thermodynamics of the system will be determined by the free energy $G = \mathfrak{E}_e + \mathfrak{E}_L - TS + pV$, where we do not include the temperature dependence of the lattice energy because one can estimate its influence to be negligibly small.

The hard core radius ρ will be determined by the occupancy of the 4*f* shell, and will thus change at the transition in a way that can be accounted for taking $\rho = \rho_0(1-\alpha n)$. One can infer from the lattice constant changes assuming complete conversion to the trivalent state $\alpha \sim 0.027$. For the interionic separation we take $R = R_0(1-\Delta)$, where Δ will include both the dependence on n and pressure.

The electronic terms E' and B are functions of the interionic separation; we take $E = E_0 - \gamma R_0 \Delta$ and B constant.[15] One reason for the variation of E has been pointed out by Kaldis and Watcher:[11] the conduction band, derived from the 5*d* levels of the Sm ions, is split by the crystal field into t_{2g} and e_g bands while the center of gravity of the hands remains at the same distance from the 4*f* levels. This splitting decreases with the wblume and thus change the energy gap between the bottom of the lowest (t_{2g}) band and the 4*f* shell.

We expand the enthalpy to second order in n and Δ. Since the approximations used to obtain the energy are rather crude, this should not introduce large error in the calculation. We can thus write $\mathcal{H} = a + b\Delta + c\Delta^2$ where the coefficients a, b, and c depend on n. The equilibrium condition $\partial G/\partial V = 0$ allows us to find the dependence of Δ on n and p:

$$\Delta = \frac{p_0 n + p}{2p_1 + p} \tag{3}$$

here

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

and

$$p_1 = \frac{Mq^2}{6R_0^3}\,\frac{1}{\rho_0} - \frac{2}{R_0}$$

(p_1 equals three times the Bulk Modulus).

Since $p_1 \sim 1200$ Kbar[9] we neglect $2p$ in the denominator of the equation for Δ. Inserting the resulting expression back into G we obtain:

$$G = G_0 + E_{eff}n + B_{eff}n^2 + kT \times \left\{n \ln n + (1-n)\ln(1-n) - n \ln \frac{Q_M}{Q_I}\right\} \tag{4}$$

where

$$E_{eff} = E_0 - \frac{Mq^2}{R} - 6\frac{R_0^3 p_0}{p_1} \cdot p = E - \Gamma p$$

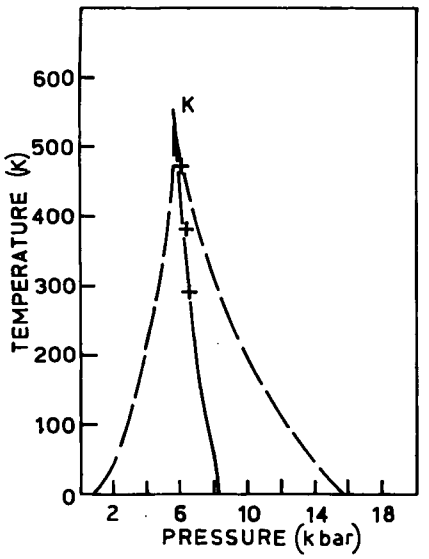

FIG. 1. p–T phase diagram for SmS. The full line represents the semiconductor–metal phase equilibrium. The broken lines are the theoretical lines of loss of stability. K indicates the critical point. Experimental data are indicated by crosses.

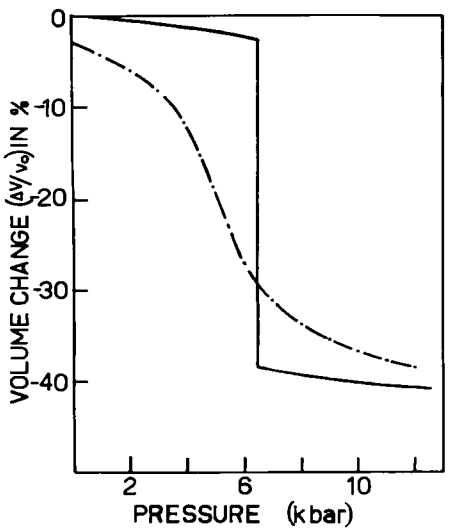

FIG. 2. Theoretical pressure–volume isotherms for SmS. Full line: room temperature. Broken line: 700°K.

and

$$B_{\mathrm{eff}} = B + \frac{3R_0^3}{p_1}(\alpha^2 p_1^2 - p_0^2)\,.$$

This expression for G is of the form given by Aptekar and Ponyatovskiy[17] from a phenomenological approach for pseudo-binary isomorphous phase transformation.

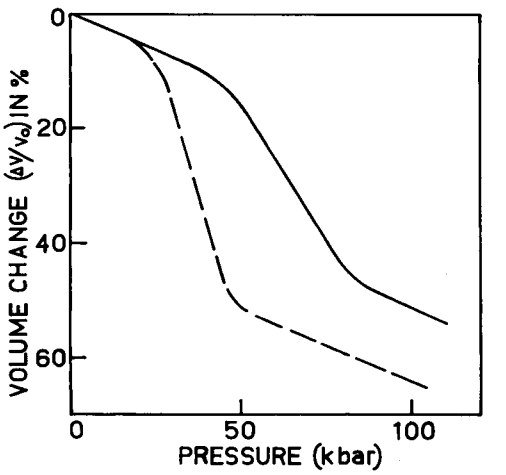

FIG. 3. Theoretical pressure–volume isotherms at room temperature for SmTe (full line) and SmSe (broken line).

The condition for thermodynamic equilibrium is that G, equation (4), should be at a minimum as a function of n. This means:

$$n = \left\{1 + \exp\frac{1}{kT}(E_{\mathrm{eff}} + 2B_{\mathrm{eff}}\, n - kT \ln Q_{\mathrm{M}}/Q_{\mathrm{I}})\right\}^{-1} \tag{5}$$

Careful consideration of the free energy shows that the type of transition[14] is determined by the sign of B_{eff}. For $B_{\mathrm{eff}} > 0$ the transition is of second order, and for $B_{\mathrm{eff}} < 0$ the transition is of first order, with a critical point, determined by $T_c = -B_{\mathrm{eff}}/2k$. Table 1 gives the values for the parameters determined from the experimental data in the following way: Γ from resistivity data;[1,2,4] p_1 from compressibility measurements,[9] p_0 from its relation to Γ and p_1; B_{eff} is determined for SmS from the transition pressure and for the other two compounds from the width of the transition region. These are taken from volume–pressure data[9] at room temperature.

Figure 1 gives the phase diagram for SmS, as determined by equations (4) and (5). The predicted critical point occurs at $p = 5.6$ kbar and $T = 554$°K. In the same drawing the metastability boundaries are also indicated. Figures 2 and 3 show the pressure–volume relation for the three compounds at room tempeature as calculated from our model. The theory gives a direct relation between the variation of the $4f$–$5d$ gap with pressure and the volume change at the transition. The

latter turns out to be bigger than it is experimentally observed for a valence change from 2 to 3. This would indicate that the valence change is in fact incomplete as conjetured by Maple and Wohlleben,[5] on a basis of lattice parameters and susceptibility data.

There has recently appeared in print a work by Herbst, Watson and Wilkins [18] in which the energies of the divalent and trivalent Sm configurations, as a function of the lattice parameter, are calculated using the renormalized atom method. These results lend support to the idea that the transition is in fact associated with a change in the $4f$ occupancy of Sm. As already pointed out in 12(a) the value for γ that we use is bracketed by the limits calculated by Herbst *et al.* We want to point out that one of the main conclusions we arrive at, namely the existence of a critical point for SmS is a consequence of the configurational entropy terms which as the temperature rises rounds off the free energy as function of n making it possible to go from an abrupt transition at low temperature to a slow transition at high temperature. The explicit form of the electronic energy part is immaterial for this to happen.

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15. Qualitatively similar dependence of the electronic energy on n have been obtained in reference (2) assuming a free electron type density of states for the band.
16. B would change because of the broadening of the band caused by volume reduction but the inclusion of this effects leads to an n^3 dependence of G through the lattice energy. If one were to include these terms the simpler linear and quadratic n dependence that arises from the square density of states should be more carefully scrutinized and a more realistic density of states s should be considered.
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Usando un modelo iónico simple para la energía de cohesión y términos electrónicos semejantes a los del modelo de Falico–Kimball para transíciones metal–aislante, se obtiene un diagrama de fases para SSm con un punto crítico a 554°K. El modelo se reduce a la teoría termodinámica propuesta por Aptekar y Ponyatovsky y permite calcular las isotermas $p-V$ para SSm, SeSm, y TeSm. Tambien se obtiene facilmente el número de agujeros en la capa $4f$ como función de presión y temperatura.