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Résumé. — Nous étudions la chaleur spécifique, la constante du réseau et les propriétés de transport des systèmes SmS-YS et SmS-SmAs. Ces matériaux présentent une transition de phase configurationnelle et une valence intermédiaire analogues à ce qui est observé dans SmS sous pression. Les résultats sont interprêtés dans le cadre d'un modèle simple de densité d'états.

Abstract. — This paper describes transport, specific heat, and lattice properties of the SmS-YS and SmS-SmAs systems. These materials exhibit a configurational phase transition and intermediate valence similar to SmS under pressure. The data is discussed in terms of a simple density of states model.

1. **Introduction.** — The systems $Sm_{1-x}Y_xS$ and $SmS_{1-x}As_x$, in analogy to pure SmS under pressure, exhibit a large volume decrease and color change, from black to gold, with increasing x [1]. Both effects are related to the proximity in energy of the $Sm\,f^5\,d$ configuration to the f^6.

It is the purpose of this paper to explore the experimental facts regarding the Y and As alloy systems, to compare these with the behaviour of SmS under pressure, and to show that many of these experiments can be interpreted in terms of a simple density of states model. This model consists of two bands, one a broad d-like conduction band, the other a very narrow band made up predominantly of Sm 4f electrons. One aspect of the model is that the Fermi energy, E_F, crosses the high density of states as well as the d band in the gold, collapsed, phase. Another important point is that the d band moves downward in energy, relative to the 4f band, with decreasing volume. The model explains the transport properties and lattice collapse. It predicts several unusual physical features, specifically a very large electronic contribution to the heat capacity and a precipitous decrease of the bulk modulus in the collapsed phase.

2. **SmS.** — In 1970 Jayaraman [2] *et al.*, discovered that, with the application of 6.5 kbars of pressure, semiconducting SmS undergoes an abrupt volume decrease of about 10 % [3] without change in its face-centered cubic crystal structure. Concomittant with this collapse, the color of the material changes from black to gold and the room temperature resistivity

decreases by approximately one order of magnitude (depending on the sample stoichiometry [4]). Furthermore, the transition is first order and is accompanied by sizeable hysteresis. Although this transition is referred to as a semiconductor to metal transition, the linear temperature dependence of the resistivity characteristic of a metal has never been observed in the high pressure phase [5]. A recent review of mixed valent compounds has been given by Varma [6].

It is generally accepted that the gross features of this pressure dependence can be explained by assuming a reaction of the form

$$Sm^{2+}(4f^6\,;\,J=0)\overset{P}{\to} Sm^{3+}(4f^5\,;\,J=5/2)+e(d,s)\,,$$
$$(1)$$
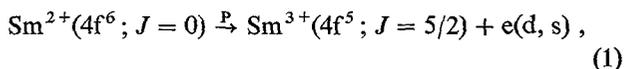
where J denotes the total angular momentum quantum number and $e(d, s)$ indicates d or s electrons. It is seen that the mechanism involves the promotion of an electron from the localized $4f^6$ configuration into the conduction band (possibly *strongly scattered*). The increase in free electron concentration, N, with pressure is consistent with the increased conductivity, σ. It is also consistent with the change in color, since the increase in plasma frequency

$$\omega_p = \left(\frac{4\,\pi Ne^2}{m^*}\right)^{1/2}\,,\qquad(2)$$

where m^* is the effective electron mass, will tend to move the reflectivity minimum to higher energies [7].

The change in ionic volume of Sm, between the divalent and the trivalent state, can be estimated from

the known lattice constants of some NaCl-type rare earth compounds [8], to be $\sim 16~\%$. This estimate supports the idea that the collapse involves a change in configuration $f^6 \to f^5 d$. Maple and Wohlleben [9] found that the magnetic susceptibility of the high pressure phase of SmS is small and temperature independent below roughly 100 K contrary to that of other cubic compounds containing Sm^{3+} in the $J = 5/2$ quantum ground state. This observation resulted in a model for SmS in which the two configurations, $4f^6$ and $4f^5 d$, of eq. (1), undergo temporal fluctuations [9] from one to the other on a timescale, τ_{df}, such that below $T \simeq 100$ K ($kT \sim \hbar\omega_{df}$) the moment of Sm^{3+} does not have a chance to develop. It was also surmised that this could only occur if the energies of the two configurations are degenerate within an energy $\Delta \sim \hbar\omega_{df}$, and that under these conditions the Sm ion is in an intermediate valence state, neither $2+$ nor $3+$. In principle these interacting states may be diagonalized and a stationary quantum mechanical ground state formed. Some progress has been made in this direction [10] but the description of the ground state remains as one of the important theoretical problems.

The first unequivocal experimental evidence for the intermediate valence state of Sm in the high pressure phase of SmS was given by Coey et al. [11, 12]. These workers reported Mössbauer absorption and isomer shift data for SmS as a function of pressure. With this microscopic technique the fact that only one absorption line is observed for all pressures means that only one species is present in the crystal and not a distribution of divalent and trivalent ions. Furthermore, the interpolation between Sm isomer shifts, which measures the electronic charge density at the Sm site, for di and trivalent compounds gives direct evidence that the Sm exists in an intermediate valence state. The value for this valence, v, defined as Sm^{v+}, is 2.7 for 7 kbars pressure [12].

Optical absorption measurements have been performed on single crystals and thin films of SmS. It has been demonstrated that, as pressure increases, the lowest optical absorption peak, $f^6 \to 4f^5 d(t_{2g})$, moves to lower energy at a rate of 10 meV/kbar [13, 14]. Here, as usual, t_{2g} indicates the lower of the two crystal field-split d-like states in an octahedral environment. This relative band motion is considered to be the source of the phase transition. Evidence for its origin in crystal field splitting rather than band broadening or electron-electron correlation effects is contained in the data of Battlogg et al. [14]. First the three t_{2g} states move downwards at 2/3 the rate that the two e_g states move upwards. Second, the lowest edge of the t_{2g} moves down at the same rate as the peak of the t_{2g}.

3. **Alloys.** — Alloys of SmS with YS, LaS, GdS, SmAs, ... develop intermediate valence at atmospheric pressure [1, 2] and eliminate the high pressure cell and make a wider variety of experiments readily available.

Since the lattice constant of YS is ~ 0.46 Å smaller than that of the isostructural SmS [1], and the estimated change in lattice constant for complete conversion to Sm^{3+} is only ~ 0.34 Å [8], YS might be expected to cause a collapse. Furthermore, Y is non-magnetic and consequently should not interfere with the Sm ion magnetic contribution to the susceptibility. The lattice constant is not, however, the only consideration. The dopant compound is also required to have a conduction band similar to the SmS conduction band. For example, even though the lattice constant of CaS is 5.689 Å, no phase transition occurs [15] because the conduction band of the alloy for all concentrations is never degenerate with the $Sm^{2+} 4f^6$ configuration. In the $Sm_{1-x}Y_x S$ alloys, each Y not only replaces a Sm in the lattice, but also donates an extra conduction electron. This is to be contrasted with SmS under pressure, where, in principle, the only free electrons are derived from valence transformed Sm ions.

$SmS_{1-x}As_x$ was chosen because it was known to collapse [16] and because arsenic acts as an acceptor in SmS. In this case the transformation is initiated by trapping a 4f electron from Sm at the As site. Extensive work on the SmGdS system has been done by Jayaraman and co-workers [17, 18], but will not be discussed here.

4. **Intermediate valence in the alloys.** — The volume strain, $e \equiv \Delta V/V \simeq 3 \Delta a/a_0$, for the three systems is given in figure 1. Here Δa is the deviation of the lattice constant from its value, a_0, for SmS. Most notable is the similarity between the three curves. Each one exhibits a lattice collapse, apparent in the abrupt
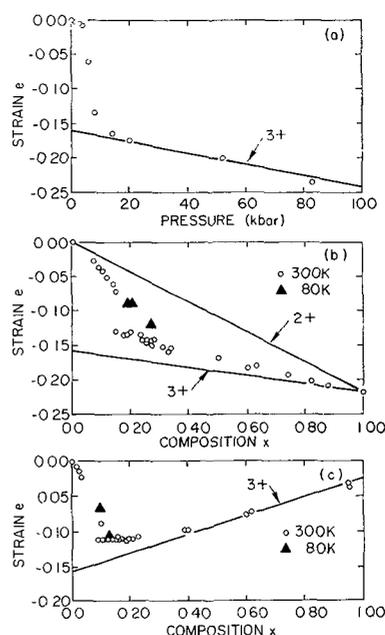

Fig. 1. — Volume strain, e, of (a) SmS versus pressure (after ref. [3]), (b) $Sm_{1-x}Y_x S$ versus composition x (after ref. [19]) and (c) $SmS_{1-x}As_x$ versus x. The lines in (b, c) represent Vegard's law for integral valence. The line in (a) which extrapolates at $P = 0$ to $- 0.16$ probably represents Sm^{3+} (Ref. [22]).

decrease in e. This collapse occurs, as can be seen from figures 1b and 1c, for much smaller concentrations in the As system.

The solid lines drawn on figures 1b and 1c represent the linear variation (Vegard's Law) of lattice constant, or e, for an alloy containing Sm either in the 2+ or 3+ state. Any large deviation from the dotted lines is anomalous and is probably an indication of intermediate valency in these systems. It appears that Sm exists only as Sm^{3+} in $SmS_{1-x}As_x$ for all $x \gtrsim 0.4$. Finally, it should be noted that the lattice collapse is temperature dependent.

Figure 1 has demonstrated that the most obvious feature, the first order lattice collapse, can be achieved by chemical means. Other experiments also confirm the similarity. The valence as determined by lattice constant [1, 19] and Mössbauer [11, 12] and X-ray photoemission (XPS) [20] measurements, is shown in figure 2. The Mössbauer isomer shift shows unambi-
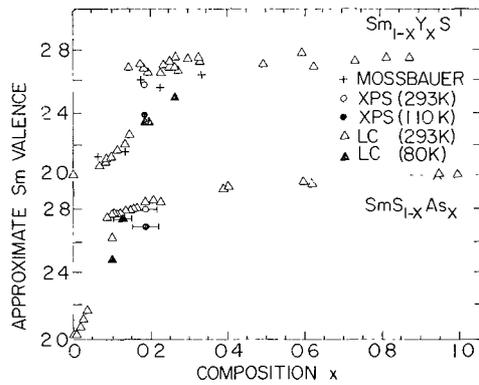

FIG. 2. — Approximate Sm valence for a) $Sm_{1-x}Y_xS$ (Ref. [19]) and b) $SmS_{1-x}As_x$ versus composition, x. Included in the graphs are values derived from measurements other than lattice constant (L C) (See Text).

guously that the valence is intermediate between 2+(f^6) and 3+(f^5d), although the actual value depends somewhat on the model. The XPS measurements show both configurations to be present, but the valence value depends both on subtracting a background and on the assumption that the surface is representative of the bulk. The valence is estimated from the lattice constant by making a linear interpolation between the measured lattice constant and the 2+ and 3+ lines drawn on figure 1. Although this method gives an estimate of v, it should be treated cautiously because the relationship between volume and valence depends on the details of the model used [21].

5. Transport properties. — In the light of the general discussions of intermediate valence we will consider the transport properties, mechanical properties, and specific heat, and will show that a simple density of states model can account qualitatively for the observed behaviour. This model is derived from the transport results, figures 3, 4 [19], 5 and 6, and the
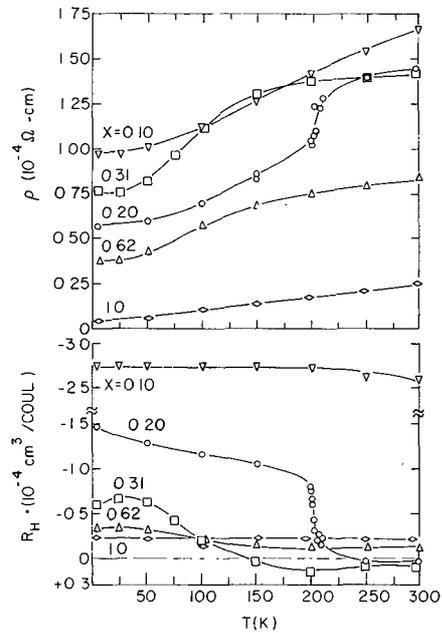

FIG. 3. — (a) Resistivity and (b) Hall constant versus temperature for various compositions x of $Sm_{1-x}Y_xS$ (Ref. [19]).

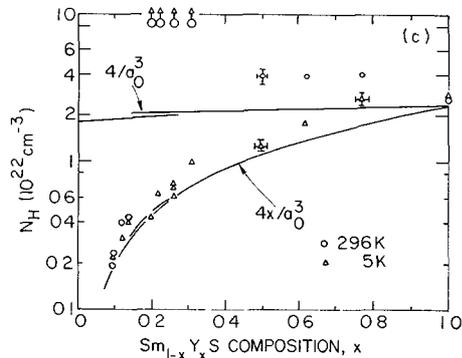

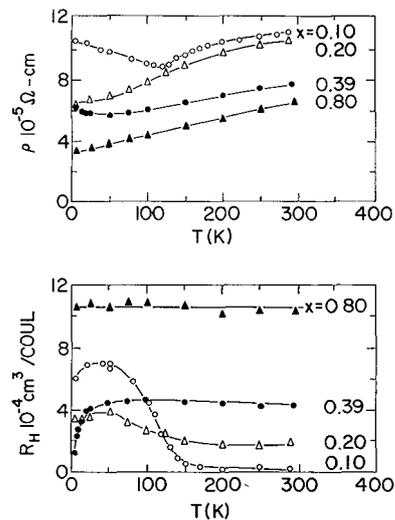FIG. 4. — Hall electron density versus composition x of the $Sm_{1-x}Y_xS$ system (Ref. [19]).

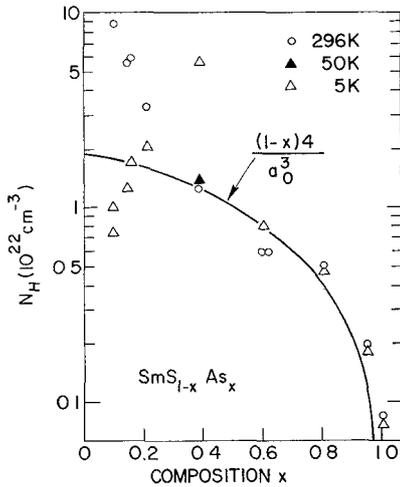FIG. 5. — (a) Resistivity and (b) Hall constant versus temperature for various compositions x of $SmS_{1-x}As_x$.

FIG. 6. — Hall electron density versus composition x of
$SmS_{1-x}As_x$.

idea that there is a drastic change in the electronic
structure due to the lattice collapse.

Figures 3a and 3b show typical resistivity, ρ, and
Hall constant, R_H, results. For black samples
($0.01 \lesssim x < 0.15$) and for pure YS ($x = 1$) the beha-
viour is metallic, that is linear ρ vs T and constant R_H.
Furthermore, for YS the carrier density, $N_H \equiv 1/R_H e$
(Fig. 4), defined in the simple one band approximation
is very close (~ 10 % higher) to that derived from the
X-ray density, $4/a_0^3$. For the black samples the N_H
values are within about 10 % of the curve $4 x/a_0^3$,
which is the electron density due to the Y donors alone.
There are two conclusions to be drawn from this data.
First, in the black phase, a simple metallic, one band
interpretation of the transport data is appropriate.
Second, the Y d-electrons are clearly seen but any Sm
f^5d contribution to the d band conductivity is small.

The behaviour in the intermediate valence state is
quite different. The $x = 0.2$ sample is black at low
temperature but collapses to the gold phase at 200 K
with an increase in ρ and a decrease in R_H. This
increase in ρ indicates that an increase in scattering
more than compensates for the increase in the number
of d electrons. The decrease in R_H which approaches
zero, indicates a breakdown of the simple one band
model. In fact, all of the gold samples have room
temperature R_H values close to zero ; some negative
and some positive.

The As transport data shows simple metallic beha-
viour for $x > 0.40$. The $x = 0.8$ data shown in figure 5,
is typical. The simple one band interpretation
$N_H = 1/R_H e$, gives the results in figure 6. On the
assumption that the Sm valence is purely 3+, as
expected from the lattice constant data, the number of d
electrons is equal to the S concentration $(1 - x) 4/a_0^3$
since each As^{3-} accepts one more electron in its valence
band than does each S^{2-}. The slight disparity between
the N_H data and the $(1 - x) 4/a_0^3$ curve is probably due
to the fact that SmAs is not a stoichiometric semi-

conductor with few carriers but a semimetal or dege-
nerate semiconductor with nearly 10^{21} carriers. The
assumption that Sm is purely Sm^{3+} is therefore a good
one for $x \gtrsim 0.4$.

The $x = 0.10$ sample shows the lattice collapse with
increasing T at about 120 K. As in the Y case, R_H falls
to a low value indicating once more a breakdown of the
simple one band model. A comparison of the ρ data,
for $x = 0.1$ and 0.2 indicates that the low temperature ρ
is higher in the black phase, contrary to the results in
the Y system. This behaviour is understandable since
in the present case there are only d electrons from the
Sm f^5d configuration and none from any Y donors.
Therefore, the carrier change dominates over the
mobility. In general, all of the collapsed samples
($0.1 < x < 0.2$) show a smaller R_H than for the pure
Sm^{3+} case, indicating a breakdown in the simple
relation $N_H = 1/R_H e$ due to a more complicated
electronic structure.

6. Model. — A density of states model (Fig. 7)
has been constructed for both alloy systems to explain
these transport data and the lattice collapse. In short
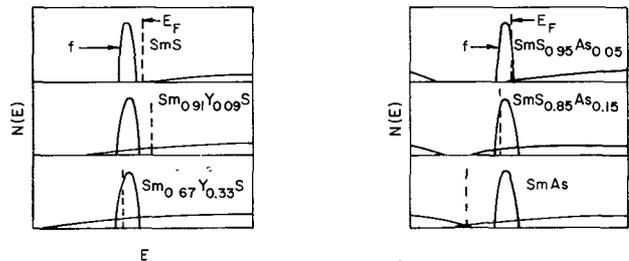the model includes a high density of states, predomi-

FIG. 7. — Suggested density of states, $N(E)$, for (a) the $Sm_{1-x}Y_xS$
(Ref. [19]) and (b) the $SmS_{1-x}As_x$ systems.

natly f^6 like, called f, and a lower density of states d
band. In the SmS-YS system, E_F cuts the d band above f
for black materials, but cuts both f and d for collapsed
gold materials. In the SmS-SmAs system the trivalent
As^{3-} causes $f^6 \rightarrow f^5$ p transitions. These As p states are
shown at the lowest energies in figure 7b. For the pure
Sm^{3+} materials E_F cuts the d band below f, but cuts
both f and d for the intermediate valence mate-
rials $x < 0.4$.

There are a number of characteristics, assumptions,
and approximations of this model.

1) It is a one electron picture applied to a many elec-
tron system. This approach is justified if one keeps in
mind that the real electronic transitions are $f^6 \leftrightarrow f^5d$
and $f^6 \leftrightarrow f^5p$ and that the one electron $f \leftrightarrow d$ and
$f \leftrightarrow p$ energies shown in figure 7 include correllation
effects. Furthermore, the f like band is taken to contain
only one electron so that it is impossible to remove
more than one electron from f^6.

2) The system is assumed to be homogeneous. All

Sm are taken as equivalent regardless of their actual environment. The assumption is probably good for large dopant concentrations but questionable at low concentrations where clustering of dopants (singlet, pairs, triplets) may have significantly different effects on their Sm neighbours [1].

3) For the case of SmS-YS there are d electrons from both the Sm f^5d configuration and from the Yd-band. For simplicity we suppose that there is a common d band for SmS-YS and all d electrons are equivalent. This is the point of view adopted for the mechanical properties [21, 22, 23]. On the other hand, the f hole of the f^5d configuration will cause strong scattering of the d electrons so that the f^5d contribution to the conductivity may be less than that of the Y d's. In addition there may be localized f^5d states for small concentrations of Y due to clustering. In fact, as has been seen, the Hall data for black SmS-YS showed no d electrons from the Sm f^5d.

4) A final characteristic is that the d band moves downward in energy relative to the f states with decreasing volume. Since this motion is primarily a crystal field effect [14], the movement of the whole band is more important than any change in shape such as broadening of the band.

7. Discussion of the model.

— It is seen from figure 7a that for pure semiconducting SmS, f is filled, and the Sm ion is in the 2 + state. As Y is added (see $Sm_{0.91}Y_{0.09}S$), the carrier concentration increases, and, because the lattice constant decreases, the conduction band moves downward with respect to f, the two merging into a complex $N(E)$. Nonetheless, E_F still lies above f due to the band filling by Y d-electrons. In this situation the Sm remains divalent, and the Hall effect measures the d band carrier concentration. The color remains black because the plasma edge, and thus the reflectivity minimum, are still in the infrared region.

The intermediate valence state has been defined as one where the Fermi energy cuts both the f and d states. This situation is shown for the sample $Sm_{0.67}Y_{0.33}S$. More Y has been added, and the material has collapsed to the gold phase. The Hall effect no longer reflects the behaviour of a simple band but depends on the shape of $N(E)$ at E_F. Furthermore, since a large density of final states for any scattering process is available, the resistivity will tend to increase. The color turns to gold because the increase in d electron concentration shifts the plasma edge into the visible [24, 25].

The lowest arsenic concentration in figure 7b depicts a very important difference between the two alloys. Whereas a relatively large amount of Y is needed to achieve the intermediate valence state, small concentrations of trivalent As will produce trivalent Sm. This means that even for very low As concentrations, E_F will

(1) Kasuya, T. Private communication.

move into the 4f states. The small radius Sm^{3+} thus produced causes the lattice to collapse at small concentrations. For large x ($\gtrsim 0.4$) f has been emptied completely. At this point the Sm is in the trivalent state and E_F lies only in the conduction band. The plot for pure SmAs suggests a semi-metallic $N(E)$ in keeping with the transport results.

The simple arguments advanced to explain the color change in the Y system are valid for As as well. In fact, SmAs reverts once more to a bluish color, in keeping with the small number of conduction electrons (Fig. 7b).

The foregoing model has been constructed to be consistent with the transport, and lattice constant data. Very similar models, with one very narrow band overlapping a conduction band, have been used to explain the properties of various actinides. Blatt [26] had derived expressions for the temperature dependences of R_H, ρ and the thermoelectric power, S [27]. Unfortunately these expressions are not applicable here because the relative band positions are not rigid in temperature. The model does, however, lend itself to a quantitative description of the elastic properties [21] which will be discussed briefly later. It also predicts a very high $N(E_F)$ for the intermediate valence state. This qualitative observation can be tested by low temperature specific heat measurements and are described below.

8. Specific heat.

— The microcalorimetric technique developed by Bachman et al. [28] was used to measure the same crystals used in the transport studies (Table I) [29]. It is possible to analyse low temperature

TABLE I

Sample	x	γ (J/mole K^2)	S (J/mol K)
$Sm_{1-x}Y_xS$			
(XXIV-100)	0	0.000 ± 0.001	~ 0.05
(74-I-66)	0.09	0.002 ± 0.001	0,
(73-I-88)	0.23	0.014 ± 0.005	$\gtrsim 0.07$
(74-I-68)	0.33	0.05 ± 0.005	~ 0.18
(XXVII-92)	1.0	0.004 ± 0.001	0
$Sm_{1-x}As_x$			
(73-I-62)	0.05		$\gtrsim 0.27$
(73-I-106)	0.15		$\gtrsim 2.5$
(74-I-112)	1.0		> 4.3
$Sm_{1-x}La_xS$			
(XXVII-34)	0.4	0.010 ± 0.002	
(XXVI-96)	1.0	0.005 ± 0.001	0

specific heat measurements into three separable terms. The specific heat is

$$C = C_m + \gamma T + \beta T^3 , \qquad (2)$$

where C_m is a magnetic contribution, and βT^3 represents the first order lattice term. For normal metals γ is proportional to $N(E_F)$.

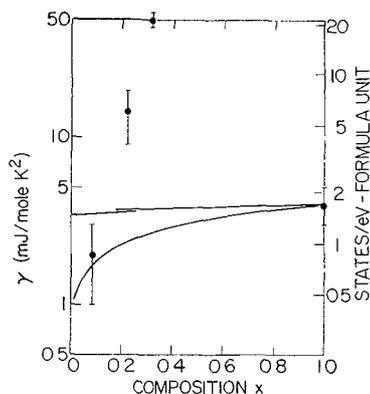The Y results for γ are presented in figure 8. The γ value for YS is comparable to that for Ti, a d-band

FIG. 8. — The coefficient of the linear term of the specific heat, γ, versus composition, x, for the $Sm_{1-x}Y_xS$ system. The curved solid line represent the variation expected for Y d-electron in a simple band. (See text and ref. [30].)

metal. The two solid curves represent the calculated d band contribution to the density of states for Sm^{2+} and Sm^{3+}. For Sm^{2+}, $\gamma \propto N(E_F) \propto x^{1/3}$ while for Sm^{3+}, $\gamma \propto N(E_F)$ is constant. Both are fit to the YS value. The order of magnitude deviation from both of these curves to higher γ for the intermediate valence compositions is obvious, and indicates the presence of a more complicated band structure and density of states. In the context of the model, this large increase is due to the enormous density of states.

In the Arsenide system the term C_m dominates the low temperature specific heat as can be seen from figure 9. This is a natural consequence of the fact that
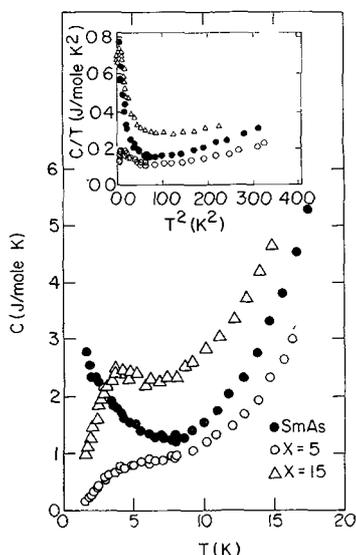

FIG. 9. — Specific heat, C, versus temperature, T, for various concentrations, x, of the $SmS_{1-x}As_x$ system. The insert shows the same family of curves with C/T versus T^2.

the Arsenide converts the Sm easily to the magnetic $Sm^{3+}(J = 5/2)$ as indicated in figure 2. Although no

estimate for γ can be made until the measurements are extended to higher temperatures, the insert, in which C/T is plotted agains T^2, demonstrates the expected trend. The 15 % sample shows the largest intercept as would be expected from figure 7.

The estimates of the excess entropy are only approximate, none the less several conclusions can be drawn. In the Y system, the entropy is certainly due to impurities, most likely Sm^{3+}. This statement is supported by the work of Walsh [30], who observed Sm^{3+} in a EPR study of SmS at atmospheric pressure. It is further corroborated by the magnetic measurements of Chouteau et al. [31], who studied the magnetic field dependence of the susceptibility up to $\sim$ 150 kOe at $\sim$ 1.4 K. They conclude that small concentrations of isolated Sm^{3+} can account for their results. Of particular note is the fact that the sample $Sm_{0.91}Y_{0.09}S$, for which the magnetic entropy is negligible (see Table I) agrees with Chouteau's [31] findings (on a similar crystal from the same batch) that the Sm^{3+} content is negligible.

The magnetic entropy for the As doped samples is high. If a $J = 5/2$ state is assumed for Sm^{3+} (no crystal field splitting) the 4 and 15 % samples contain a calculated Sm^{3+} content of 1.8 and 16 % respectively (see Table I). The implications of the latter result are that every As produces approximately one trivalent Sm. The remaining Sm ions are in the intermediate valence state.

9. **Mechanical properties.** — The lattice collapse and bulk modulus are discussed in more detail elsewhere [20]. There are, however, conclusions relevant to this work. First of all the lattice collapse occurs because for some conditions the system is unstable to transition from f^6 to f^5d. This instability occurs because the f^5d energy decreases with decreasing volume and Sm^{3+} is smaller in size than Sm^{2+}. Similarly, if the lattice constant is decreased due to pressure, the f^5d energy is lowered favoring an increase in f^5d

TABLE II

Sample	x	B kbar
$Sm_{1-x}Y_xS$	—	—
XXVI-102	0	475
74-I-66	0.09	442
74-II-108	0.25	71
74-II-110	0.28	122
74-II-32	0.8	796
XXVII-24	1	998
$SmS_{1-x}As_x$		
XXVI-102	0	475
74-I-98	0.005	322
74-I-36	1	783
$Sm_{1-x}La_xS$		
XXVI-102	0	475
XXV-112	0.05	412
75-II-100	0.3	210
XXVII-34	0.4	174
XXVI-96	1	836

population, a further lowering of the f^5d electron energy thus causing additional volume decrease ; that is the lattice appears soft. Thus, if zero energy transitions between f^6 and f^5d are allowed (intermediate valence, degenerate configuration case) then the lattice will be soft. If the configuration does not change with pressure (integral valence, non-degenerate case), however, the lattice will have its normal stiffness. The bulk modulus is therefore a test for intermediate valence. Our results are given in table II. It can be seen that the $Sm_{1-x}Y_xS$ samples for $x = 0.25, 0.28$ and 0.8, the $SmS_{1-x}As_x$ for $x = 0.005$ and the SmLaS for $x = 0.3$ and 0.4 are softer than the simple average values one might expect. The reason is that they are intermediate valent, as one would infer from the lattice constant.

10. **Susceptibility.** — The susceptibility of intermediate valence compounds and alloys have been discussed by Maple and Wohlleben [9, 32] and more recently by Varma [6]. Tao and Holtzberg [33] have studied the susceptibility in the Y system. Suffice it to say that SmYS exhibits the same characteristic lack of moment at low temperatures found for SmS under pressure. This is not the case for the SmSAs alloys [34] which have a more complicated and, as yet unexplained, temperature dependent magnetization Sales and Wohlleben [35] have successfully made a quantitative fit of the temperature dependent susceptibility of several Yb compounds using the idea of interconfigurational fluctuations. Sales and Viswanathan [36] extended this analysis to a variety of $RE-Cu_2Si_2$ compounds. Although these latter results provide an excellent empirical description of the data, a microscopic quantitative theory has not yet been developed. Varma and Yafet [10] have, however, obtained expressions for the susceptibility which agree qualitatively with experiment and Stevens [37] has recently advanced

argument based on symmetry consideration for obtaining a $J = 0$ ground state in the collapsed phase of SmS.

11. **Excited states.** — For intermediate valence situations, an interesting comparison can be made between experiments which depend on the ground state only and those which depend on the excited states as well. In general the experiments which measure ground state properties yield results which are an average of those expected from the individual configurations (isomer shift [11, 12], lattice constant [1, 2, 19]) or some new behaviour which depends on details of the actual ground state (magnetic susceptibility [9, 33], transport [5, 19], bulk modulus [18, 20, 21]). On the other hand the spectroscopic experiments see the individual configurations themselves and not average properties. The reason for this distinction is that although the ground states of the individual configurations are degenerate the excited states are not. Therefore in experiments where the excited states are final states (optical properties [14, 26], photoemission [20, 38], or intermediate states (nearly resonant Raman [39, 40])) the individual configurations are probed.

12. **Conclusion.** — The properties of SmS, SmS-YS, SmS-SmAs in their collapsed intermediate valence state have been compared. This behaviour has been contrasted to that for integral Sm valence. In the intermediate valence case, increased scattering is found in transport, the electronic contribution to the specific heat is anomalously large and the bulk modulus is considerably reduced. The results are explained in terms of a density of states model.

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