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Intermediate valence in $SmSb_xS_{1-x}$ alloys

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Results are presented for lattice-parameter and magnetic-susceptibility measurements on a series of solid solutions $SmSb_xS_{1-x}$. Low-temperature magnetic-susceptibility measurements indicate an inhomogeneous mixed valence for alloys containing low antimony concentrations and a homogeneous intermediate valence at larger concentrations. The susceptibilities of antimony-rich samples illustrate the disappearance of the antiferromagnetic ordering observed in pure SmSb. The alloys of intermediate composition display a nonmagnetic ground state associated with intermediate valence of the samarium cations. The effect of slight sulfur substitution in SmSb on crystalline electric fields is also discussed.

I. INTRODUCTION

The samarium monochalcogenides (SmX, where X = S,Se,Te) have attracted increasing attention to their intermediate valence behavior since the first reports[1-3] of pressure-induced semiconductor-to-metal transitions in these compounds. The transitions observed in SmSe and SmTe were continuous, whereas SmS exhibited a spectacular discontinuous transition from a black semiconducting phase to a golden metallic phase at 6.5 kbar. The transition in SmS is accompanied by a discontinuous isostructural contraction of the NaCl-type crystal owing to the smaller cationic radius of $Sm^{3+}(4f^5$ configuration). The results of lattice parameter measurements[4] and optical studies[5] provided an estimate of ~2.8 for the average samarium valence in the "collapsed" gold phase of SmS.

Investigations into the electrical,[2,6,7] optical[3,5,7-9] thermal,[6,10] and magnetic[4,11] properties of SmS in both the semiconducting and metallic phases helped to establish the nature of the electronic transition. A most intriguing result of the magnetic susceptibility measurements[4] performed on metallic SmS was the apparent nonmagnetic ground state exhibited by the material. An admixture of Sm^{3+} ions in the metallic phase might have been expected to contribute either a Curie-like behavior or magnetic ordering at low temperatures as a result of the $^6H_{5/2}$ ground state of trivalent samarium. However, the susceptibility was found to saturate to a constant value as $T \rightarrow 0$ with no evidence of antiferromagnetic ordering from room temperature to 1 K.

The collapsed gold phase of SmS can be stabilized at atmospheric pressure[12-17] through the process of alloying the compound with a number of other rare-earth monosulfides. Although many of the properties exhibited by the alloys are analogous to those observed in pressurized SmS, the two processes are not strictly equivalent. The size[16,18] of the substitute ion in the alloy was shown not to be the sole determinant of lattice collapse. Substantial differences have been observed between the two series of alloys, $Sm_{1-x}Yb_x^{2+}S$ and $Sm_{1-x}Nd_x^{3+}S$. Although the lattice parameter of divalent YbS is smaller than that of trivalent NdS, Yb substitution in SmS failed to initiate a lattice collapse while Nd substitution caused a collapse at ~15-at.% Nd. Clearly, the electronic structure of the substitute cation is crucial in the determination of lattice collapse in alloy systems of SmS.

In addition to cation substitution, the collapsed phase has been observed in the anion-substituted system[12,14] $SmAs_xS_{1-x}$. The samarium ion is trivalent in SmAs and the compound seems to be a semimetal. From the observed lattice collapse in the solid solutions, the samarium valence appears to increase with increasing As concnetration x from divalent in SmS to trivalent for $x \geqslant 0.4$. There is a very abrupt change in volume at $x \simeq 0.05$ indicating a change in the samarium valence from 2.2 to 2.8. Here, as in the cation substituted alloys, it is clear that the electronic properties of the substitute ion plays an essential role in inducing the collapsed state. With the As substitution the trivalent character of the ion is being exploited. However, the size of the substitute ion is also expected to be important. The As^{3-} has significantly larger ionic radius than S^{2-}, however the lattice parameter of $Sm^{3+}As$ is ~1% smaller than that of $Sm^{2+}S$.

This observation of intermediate valence in the

$SmS_{1-x}As_x$ solid solutions suggests the study of solid solutions of SmS with the other samarium monopnictides. Here we present the results of lattice parameter and magnetic susceptibility measurements for the $SmSb_xS_{1-x}$ solid solutions. The samarium ion is also trivalent in SmSb and the compound exhibits only a slightly more metallic character than SmAs. However the Sb^{3-} ion is sufficiently larger than the AS^{3-} that the lattice constant of $Sm^{3+}Sb$ is 5% larger than that of $Sm^{2+}S$. Therefore a comparison of the $SmSb_xS_{1-x}$ and $SmAs_xS_{1-x}$ systems is of interest.

II. EXPERIMENTAL METHODS

Alloy samples for this investigation were prepared in the following manner. The initial reaction of the elements in sealed evacuated (10^{-7}-mm) quartz tubes was controlled by a slow heating (~1 deg/min) to 500 °C. The reaction was continued at this temperature for 18 h at which time the temperature was set to 850 °C for an additional 2 h before cooling. The inhomogeneous product of this reaction was then transferred to a small tantalum capsule and sealed under vacuum (10^{-3}mm). After induction heating to ~2100 °C, the sample was quenched from the melt.

It was found that a slow cooling from 2100 °C occassionally resulted in phase separation as evidenced by broadened x-ray diffraction lines. The process of quenching permitted uniform solid solutions to be prepared throught much of the alloy composition range. However, our alloys of $SmSb_xS_{1-x}$ in the region $0.20 \leq x \leq 0.40$ proved to be multiphase and, consequently, are not included in the present report.

Lattice parameter measurements of the alloy samples were obtained with a Guinier–de Wolff focusing camera using Cu $K\alpha$ radiation and an internal ThO_2 standard. Lattice parameters within ±0.01 Å were readily obtainable with this arrangement. More-precise measurements (±0.001 Å) were performed on SmS and SmSb with a 114.6-mm Debye-Scherrer cylindrical camera offering high resolution in the back-reflection region. In addition, modifications in this camera permitted low-temperature x-ray measurements to 77 K. Cooling was achieved through the controlled flow of vaporizing nitrogen across the sample capillary, and temperature was monitored by a chromel-alumel thermocouple in close proximity to the sample.

The magnetic-susceptibility apparatus, described elsewhere,[19] operates in the temperature interval 1.5 to 300 K. Thermal stability is generally ±0.3 K near room temperature, improving to ±0.05 K below 4.2 K. Typical errors associated with measured gram susceptibilities have been found to be within 1.5%. Systematic errors in computed molar susceptibilities arising from possible variations in the reported compositions are not expected to exceed 1% based on the small difference between the mass of sample after reaction and that of the starting elements.

III. LATTICE PARAMETER VERSUS COMPOSITION

The dependence of the alloy lattice parameter on composition is illustrated in Fig. 1. The values obtained for SmS (5.970 Å) and SmSb (6.269 Å) are in agreement with those previously reported.[20] No apparent discontinuity in the alloy lattice parameter is observed with the available data. Although no gold phase samples were attained in the preparation of $SmSb_xS_{1-x}$ alloys, the samples in the composition range $0.45 \leq x \leq 0.85$ exhibited a more metallic, silvery luster than was evident in either SmS or SmSb.

An estimate of the average samarium valence in an alloy sample may be deduced from the measured lattice parameter when a model of hard-sphere mixing of Sm^{2+}, Sm^{3+}, S^{2-}, and Sb^{3-} ions is assumed for the lattice.[14] A lattice parameter of 5.62 Å for $Sm^{3+}S$ has been interpolated from the lattice parameters[21] of neighboring trivalent rare-earth sulfides. Designating a_2 and a_3 as the lattice parameters of $Sm^{2+}S$ and $Sm^{3+}S$, respectively, the average samarium valence of the anion-substituted alloy $SmSb_xS_{1-x}$ is obtained from

$$v(x) = (2+x) + \frac{a_2 - a(x) - x[a_2 - a(x=1)]}{a_2 - a_3} .$$

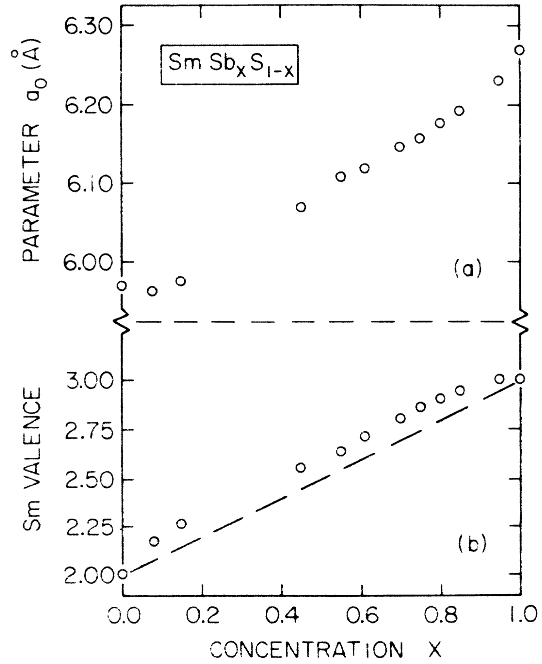

FIG. 1. (a) Lattice parameter vs concentration and (b) average samarium valence as calculated from lattice parameters vs concentration in the alloy system $SmSb_xS_{1-x}$.

The first term $(2+x)$ represents the inherent effect of the substitution of trivalent anions. Electrons released by the samarium cations, according to this term, become localized at the Sb^{3-} sites. The second term, however, provides a measure of the nonbonding electrons present in the alloy sample. It is calculated from the observed deviation of the lattice parameter from Vegard's rule. This term gives an estimate for the number of electrons delocalized through the mechanism, $4f^6 \rightarrow 4f^5$ +conduction electron.

The dependence of the average samarium valence on alloy composition is also shown in Fig. 1. The valence deduced from lattice-parameter measurements effectively sturates to 3+ at the antimony concentration $x \sim 0.95$. In addition, the existence of nonbonding electrons in a concentration of ~0.1 electron per samarium is indicated for nearly the entire alloy composition range. The absence of a gold phase is seen as the consequence of an insufficient concentration of conduction electrons to move the reflectivity minimum to high enough energies in any of our alloy samples.

IV. MAGNETIC SUSCEPTIBILITY VERSUS COMPOSITION

Room-temperature magnetic-susceptibility measurements of the $SmSb_xS_{1-x}$ alloys provide an additional estimate for the average samarium valence as it varies with antimony concentration. The susceptibility data in Fig. 2 display a number of interesting features. An initial increase in magnetic susceptibility is seen to occur at low antimony concentrations. A similar effect[4,17] has been reported in pressurized SmS for pressures up to 6.5 kbar and has also been observed in the cation-substituted systems $Sm_{1-x}La_xS$ and $Sm_{1-x}Y_xS$ for small x. An enhancement of the exchange interactions between Sm^{2+} ions owing to the introduction of conduction electrons into the crystal lattice has been proposed to explain this effect.

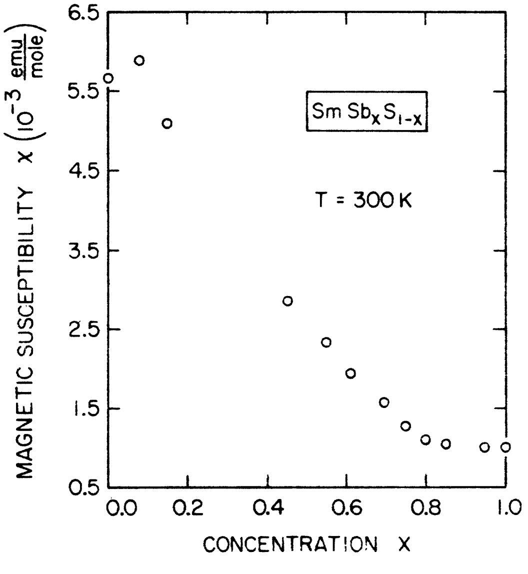

FIG. 2. Room-temperature magnetic susceptibility vs alloy concentration for the system $SmSb_xS_{1-x}$.

The magnetic susceptibilities of the alloys containing high antimony concentrations indicate that samarium trivalency is effectively achieved at a concentration $x \sim 0.85$. This value differs slightly from the corresponding result obtained using lattice parameter data. However, the two methods appear, for the most part, to yield consistent results.

Finally, it should be noted that the general trend in the magnetic-susceptibility values of Fig. 2 indicates that a continuous change in samarium valence through the composition range of poor miscibility appears likely. This is similar to the results observed in the lattice-parameter measurements.

V. MAGNETIC SUSCEPTIBILITY VERSUS TEMPERATURE

Figure 3 illustrates our measured thermal dependence of magnetic susceptibility for SmS, SmSb, and several of their mutual solid solutions in the temperature interval 1.5–300 K. SmS exhibits an exchange enhanced[11] Van Vleck susceptibility associated with divalent samarium in which the $J=0$ ground state is separated by 421 K from the first excited state $(J=1)$. A Curie-like rise in susceptibility at the lowest temperatures is attributed to a small amount (<1%) of Sm^{3+} in the lattice and to possible impurities of other rare earths. Iron impurities, found to exist in the ori-

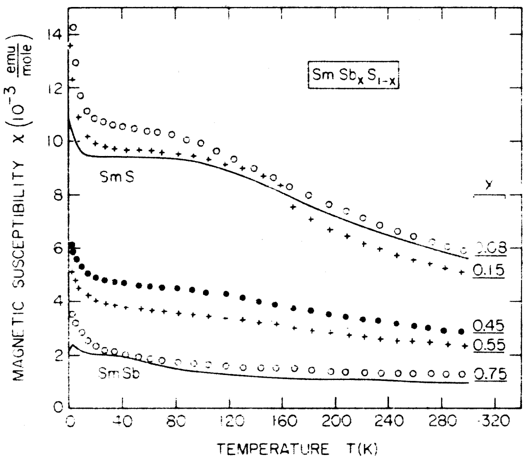

FIG. 3. Magnetic susceptibility vs temperature from 1.5 to 300 K for SmS (upper solid line), SmSb (lower solid line), and alloys of concentration $x=0.08$, 0.15, 0.45, 0.55, 0.75 in the system $SmSb_xS_{1-x}$.

ginal samarium metal[22] in a concentration under 0.006 at. %, should not contribute significantly to this effect.

The magnetic susceptibility of SmSb reveals several features associated with the Sm^{3+} ions present in the crystal. The material exhibits an antiferromagnetic transition at $T_N = 2.8 \pm 0.1$ K. An additional anomaly in the magnetic susceptibility appears near 30 K which is interpreted as the result of crystalline electric field effects. Specific-heat studies[23,24] of SmSb have demonstrated a corresponding Schottky anomaly at that temperature. The cubic crystal field in SmSb splits the $J = \frac{5}{2}$ ground-state manifold of Sm^{3+} into a Γ_7 doublet and a Γ_8 quartet, separated by ~65 K. A suppression of magnetic susceptibility as compared with the free-ion Curie law is expected to become significant at temperatures below approximately one-third the crystal-field splitting.[25] At high temperatures, Curie-law behavior is not apparent owing to Van Vleck paramagnetism and the increasing population of higher moment ($J = \frac{7}{2}$) states.

A comparison of the low-temperature magnetic susceptibilities among the $SmSb_xS_{1-x}$ alloys indicates that a substantial enhancement in the Curie-like rise below 20 K exists in alloys containing small antimony concentrations. Although not shown in Fig. 3, the magnetic susceptibility of $SmSb_{0.08}S_{0.92}$ rose to 17×10^{-3} emu/mole at the lowest temperature attained (1.5 K). It is expected that Sm^{3+} ions stabilized near the Sb^{3-} sites in dilute alloys are responsible for the enhanced Curie rise. It is not surprising that local environment effects can be very important in the anion-substituted alloys, particularly in the dilute range. This interpretation of the susceptibility data as evidence for nonhomogeneous mixed valence in dilute alloys is supported by electrical and magnetic studies[26] of the $SmAs_xS_{1-x}$ system which indicated the existence of Sm^{3+} clusters centered on the As^{3-} anions for $x < 0.05$.

A small anomaly in the magnetic susceptibility of $SmSb_{0.15}S_{0.85}$ near 160 K appears similar to larger anomalies observed in samples of other SmS alloy systems[12,13,19] which undergo a temperature-induced valence change. These alloys exhibit a corresponding lattice-parameter anomaly and, in the case of first-order transitions, show a thermal hysteresis effect. Lattice-parameter measurements of $SmSb_{0.15}S_{0.05}$ in the temperature range 90–300 K, however, did not indicate any substantial variation near 160 K, except for the expected lattice contraction with decreasing temperature. No significant hysteresis was discernable in magnetic susceptibility under thermal cycling. It is clear that any possible temperature-induced valence transition in this sample must be quite small and continuous. The problem of miscibility in solid solutions where $0.20 \leq x \leq 0.40$ is indeed unfortunate since alloys in this composition range might be expected to offer significant contributions concerning this phenomenon.

The alloys containing high antimony concentrations exhibit magnetic susceptibility curves which indicate the existence of intermediate valence at the samarium sites. The samples $SmSb_{0.45}S_{0.55}$ and $SmSb_{0.55}S_{0.45}$, for instance, show neither magnetic ordering nor substantial paramagnetic divergence at low temperatures. The susceptibility of $SmSb_{0.75}S_{0.25}$ shows a slight decrease below 2.8 K which is not apparent in Fig. 3. The existence of magnetic ordering in our alloys is discussed in Sec. VI.

An intriguing feature observed in the low-temperature magnetic susceptibility of antimony-rich alloys is the disappearance of crystalline electric field effects which are present in pure SmSb. The susceptibility data presented in Fig. 3 show that the effect of crystal fields has vanished in the $SmSb_{0.75}S_{0.25}$ sample. Measurement of additional alloy samples at temperatures below 80 K clearly reveals the disappearance of crystal-field effects with as little as 5% sulfur substitution in the SmSb lattice as illustrated in Fig. 4. Since the $4f$ level is at the Fermi energy when there is intermediate valence, one should expect a significant effect on the crystal-field splitting of the $J = \frac{5}{2}$ ground state of trivalent samarium. However, the crystal field effects are seen to vanish even in the $SmSb_{0.95}S_{0.05}$ alloy where lattice-constant and room-temperature susceptibility measurements suggest the samarium ions are all trivalent. Therefore, it is not clear whether the disappearance of crysal-field effects is attributable to intermediate valence or to the extra conduction electrons contributed by the sulfur acting as donors in SmSb. Electrical measurements are planned which will investigate the effect of sulfur substitution in the SmSb lattice.

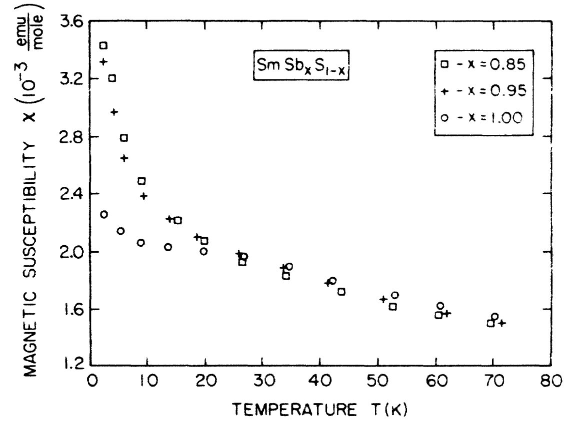

FIG. 4. Magnetic susceptibility vs temperature from 2.8 to 70 K for alloys of concentration $x = 0.85$, 0.95, 1.00 in the system $SmSb_xS_{1-x}$.

VI. MAGNETIC ORDERING

The occurrence of an antiferromagnetic transition in pure SmSb provides an excellent opportunity to experimentally observe the effect of intermediate valence on magnetic ordering. Mott[27] has discussed the conditions under which ordering may be expected to occur in systems which exhibit intermediate valence assuming the $4f$ electrons form a narrow band at the Fermi energy. Ordering is most likely to happen if the mean number of electrons on each ion differs by no more than a small number Δn from an integer. Then the lifetime of the residual moment at the ionic site is given by $\tau \sim \hbar/I\Delta n$, where I is the overlap energy integral for $4f$ orbitals on neighboring sites in Mott's discussion, but might also include the effects of hybridization with the valence band. If $I\Delta n$ is less than the magnetic-coupling energy for adjacent ions, then magnetic ordering should be observed. In pressurized SmS, where a samarium valence of ~2.8 is obtained, no magnetic ordering has been found.

The effect of sulfur substitution into the SmSb lattice on magnetic ordering is illustrated in Fig. 5. The rather large difference in the low-temperature susceptibilities of SmSb and $SmSb_{0.95}S_{0.05}$ is the result of crystal fields discussed in Sec. III. The disappearance of magnetic ordering with increasing sulfur content is evidenced by a noticeable rounding of the susceptiblity cusp and a trend toward the leveling of susceptibility at temperatures below 2.8 K. All measured alloys with antimony concentration $x \geq 0.75$ exhibited a maximum susceptibility at $T = 2.8 \pm 0.1$ K. The data clearly indicate that the ordered antiferromagnetic state is destroyed by sulfur substitutions as small as 15% where the samarium is very nearly trivalent. Mössbauer measurements on samples in this composition range may establish this more precisely. The susceptibilities of samples where $x \lesssim 0.70$ are similar to those observed in pressurized SmS and chemically collapsed $Sm_{1-x}Y_xS$. The nonmagnetic ground state of $SmSb_{0.55}$S0.45 is apparent in Fig. 5 since its susceptibility shows no evidence of magnetic ordering and is seen to saturate to finite value as $T \rightarrow 0$.

VII. CONCLUSION

Strong evidence for the intermediate-valence configuration in $SmSb_xS_{1-x}$ solid solutions is provided by the lattice parameter and magnetic susceptibility measurements. The intermediate valence state of the samarium cations results purely from chemical alloying in this system. The large size of substitute Sb^{3-} anions in SmS appears to prohibit a collapse to the gold phase as observed in arsenic-substituted SmS.

The SmS alloys with dilute concentrations of Sb exhibit an inhomogeneous mixed valence state. Some evidence for the possible existence of excitonic-type states[28] in these alloys has been found. The estimates of the number of nonbonding electrons in these alloys according to lattice parameter data were comparable to those calculated for the samples containing higher antimony concentrations (~0.1 electron/samarium). However, preliminary resistance measurements on small, irregularly shaped alloy crystals indicate that a substantial difference may exist in electrical conductivities between the two groups of alloys. $SmSb_xS_1$ samples in the composition range $x \geq 0.45$ exhibit metallic conductivities consistent with their silvery appearance, while the conductivities of $SmSb_{0.08}S_{0.92}$ and $SmSb_{0.15}S_{0.85}$ appear comparable to semiconducting SmS.

The low-temperature magnetic susceptibilities of $SmSb_xS_{1-x}$ alloys indicate a homogeneous intermediate valence in alloys containing antimony concentrations $0.45 \lesssim x \lesssim 0.85$. The antiferromagnetism observed in SmSb seems to disappear with the occurrence of intermediate valence. We believe that the magnetic-susceptibility data obtained in this investigation which illustrate the disappearance of magnetic ordering in the $SmSb_xS_{1-x}$ alloys is the first such evidence presented for any samarium compound. We plan to prepare additional samples in the composition range $0.85 \leq x \leq 1.0$, and perform Mössbauer measurements to test the predictions of Mott[27] for the occurrence of magnetic order in intermediate valence compounds.

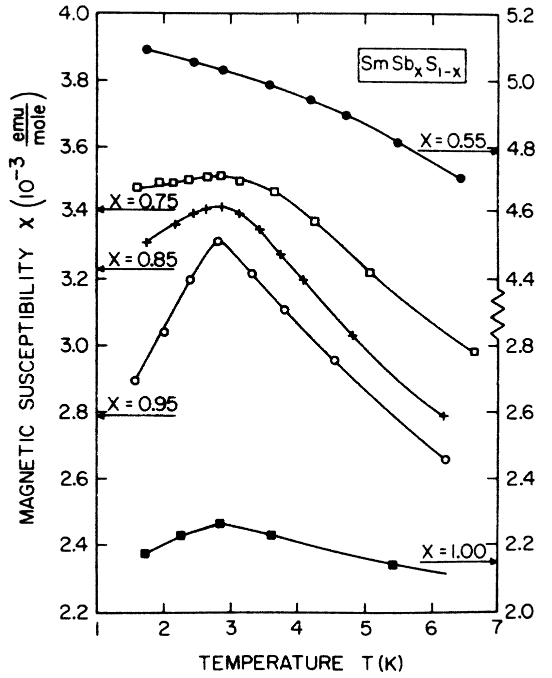

FIG. 5. Magnetic susceptibility vs temperature from 1.5 to 7 K for alloys of concentration $x = 0.55$, 0.75, 0.85, 0.95, 1.00 in the system $SmSb_xS_{1-x}$. The right ordinate refers to the $x = 0.55$ alloy (top) and SmSb (bottom). The left ordinate refers to the three remaining alloys.

[1] A. Jayaraman, V. Narayanamurti, E. Bucher, and R. G. Maines, Phys. Rev. Lett. 25, 368 (1970).

[2] A. Jayaraman, V. Narayanamurti, E. Bucher, and R. G. Maines, Phys. Rev. Lett. 25, 1430 (1970).

[3] E. Bucher, V. Narayanamurti, and a. Jayaraman, J. Appl. Phys. 42, 1741 (1971).

[4] M. B. Maple and D. Wohlleben, Phys. Rev. Lett. 27, 511 (1971).

[5] B. Batlogg, E. Kaldis, A. Schlegel, and P. Wachter, Phys. Rev. B 14, 5503 (1976).

[6] S. D. Bader, N. E. Phillips, and D. B. McWhan, Phys. Rev. B 7, 4686 (1973).

[7] D. W. Pohl, R. Jaggi, K. Gisler, and H. Weibel, Solid State Commun. 17, 705 (1975).

[8] E. Kaldis and P. Wachter, Solid State Commun. 11, 907 (1972).

[9] J. L. Kirk, K. Vedam, V. Narayanamurti, A. Jayaraman, and E. Bucher, Phys. Rev. B 6, 3023 (1972).

[10] T. G. Ramesh and V. Shubba, Solid State Commun. 19, 591 (1976).

[11] S. M. Shapiro, R. J. Birgeneau, and E. Bucher, Phys. Rev. Lett. 34, 470 (1975).

[12] F. Holtzberg, AIP Conf. Proc. 18, 478 (1974); S. Von Molnar, T. Penney, and F. Holtzberg, J. Phys. Colloq. 37, C4-241 (1976).

[13] A. Jayaraman, E. Bucher, P. D. Dernier, and L. D. Longinotti, Phys. Rev. Lett. 31, 700 (1973).

[14] R. A. Pollak, F. Holtzberg, J. L. Freeouf, and D. E. Eastman, Phys. Rev. Lett. 33, 820 (1974).

[15] T. Penney and F. Holtzberg, Phys. Rev. Lett. 34, 322 (1975).

[16] A. Jayaraman, P. Dernier, and L. D. Longinotti, Phys. Rev. B 11, 2783 (1975).

[17] L. J. Tao and F. Holtzberg, Phys. Rev. B 11, 3842 (1975).

[18] E. Bucher, cited in Ref. 16.

[19] F. B. Huck, Wm. R. Savage, and J. W. Schweitzer, Phys. Rev. B 8, 5213 (1973).

[20] A. Iandelli, in *Rare Earth Research,* edited by E. V. Kleber (Macmillan, New York, 1961), p. 135.

[21] E. Bucher, K. Andres, F. J. DiSalvo, J. P. Maita, A. C. Gossard, A. S. Cooper, and G. W. Hull, Jr., Phys. Rev. B 11, 500 (1975).

[22] R. B. Beeken and Wm. R. Savage, Phys. Rev. B 15, 5307 (1977).

[23] R. J. Birgeneau, E. Bucher, J. P. Maita, L. Passell, and K. C. Turberfield, Phys. Rev. B 8, 5345 (1973).

[24] M. E. Mullen, B. Lüthi, P. S. Wang, E. Bucher, L. D. Longinotti, J. P. Maita, and H. R. Ott, Phys. Rev. B 10, 186 (1974).

[25] G. Williams and L. L. Hirst, Phys. Rev. 185, 407 (1969).

[26] F. Holtzberg, O. Pena, T. Penney, and R. Tournier, Abstract of Poster from International Conference on Valence Instabilities and Related Narrow Band Phenomena, University of Rochester, 1976 (unpublished).

[27] N. F. Mott, Philos. Mag. 30, 403 (1974).

[28] T. Kasuya, J. Phys. Colloq. 37, C4-261 (1976).