

## Thermal Conductivity of $\text{Sm}_3\text{S}_4$ System with Mixed Valence Sm Ions<sup>1</sup>

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The thermal conductivity ( $\kappa$ ) and electrical resistivity ( $\rho$ ) of mixed-valence compound  $\text{Sm}_3\text{S}_4$  have been measured in the temperature range 5 to 300 K. The present results and those presented previously [1] for the thermal conductivity between 80 to 850 K are interpreted in terms of the temperature-dependent fluctuating valence of Sm ions.  $\text{Sm}_3\text{S}_4$  crystallizes in the cubic  $\text{Th}_3\text{P}_4$  structure, and the cations with different valences occupy equivalent lattice sites. Divalent and trivalent Sm ions are randomly distributed in the ratio of 1:2 over all possible crystallographic cation positions ( $\text{Sm}_2^{2+}\text{Sm}_2^{3+}\text{S}_4^{-}$ ). The behavior of the  $\text{Sm}_3\text{S}_4$  lattice thermal conductivity  $\kappa_{\text{ph}}$  is extraordinary since valences of Sm ions are fluctuating ( $\text{Sm}^{3+} \rightarrow \text{Sm}^{2+}$ ) with a temperature dependent frequency. In the interval 20 to 50 K (low “hopping” frequencies),  $\kappa_{\text{ph}}$  of  $\text{Sm}_3\text{S}_4$  varies as  $\kappa_{\text{ph}} \sim T^{-1}$  (it is similar to materials with static distribution of cations with different valences): at 95 to 300 K (average “hopping” frequencies  $10^7$  to  $10^{11}$  Hz),  $\kappa_{\text{ph}}$  changes as  $\kappa_{\text{ph}} \sim T^{-0.3}$  (it is similar to materials with defects). Defects in  $\text{Sm}_3\text{S}_4$  appear because of local strains in the lattice by the electrons hopping from  $\text{Sm}^{2+}$  ions (with big ionic radii) to  $\text{Sm}^{3+}$  ions (with small ionic radii) and back ( $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$ ), at  $T > 300$  K (high “hopping” frequencies),  $\kappa_{\text{ph}}$  becomes similar to materials with homogenous mixed valence states [1].

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**KEY WORDS:** electrical resistivity; mixed-valence compound; thermal conductivity.

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## 1. INTRODUCTION

Researchers in many laboratories of the world still have interest in the behavior of the thermal conductivity in compounds with mixed (intermediate) valence (MV) [1–3]. The MV phenomenon is accounted for by the rare-earth (RE) ions in these compounds. All intermediate-valence materials can be divided into three groups according to the crystallographic positions the RE ions occupy, as well as to the nature of their electronic relation [2]. The first two of these groups (Ia and Ib) combine compounds whose RE ions sit at crystallographically equivalent sites in the lattice. In materials of group Ia, the  $4f$  electrons transfer between RE-ion configurations with different average numbers of electrons at the center, i.e., with different valences [transition between the  $4f^n$  and  $4f^{n-1} + (sd)$ ]. The frequency of these transitions does not depend on temperature and is  $\cong 10^{15}$  Hz. These materials are called compounds with homogeneous MV. Materials of group Ib exhibit electron hopping between cations in different valence states with a temperature-dependent frequency from zero to  $\cong 10^1$  Hz (at 300 K). Such systems are referred to as materials with *inhomogeneous* MV. Finally, the third group includes compounds in which cations in different valence states occupy nonequivalent crystallographic lattice sites, with no electron hopping between them. Such systems bear the name of materials with static MV.

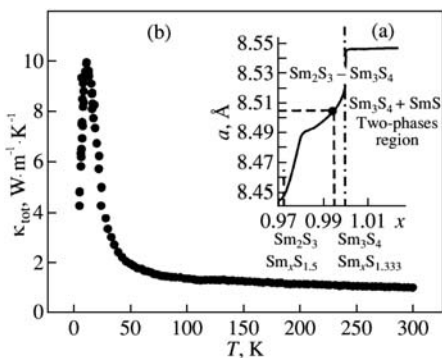
Materials with homogeneous MV are exemplified by  $\text{SmB}_6$ ,  $\text{SmS}$  (under hydrostatic pressure) and  $\text{Sm}_{1-x}\text{Ln}_x$  ( $\text{Ln} = \text{Gd}, \text{Y}, \text{etc.}$ ). The literature does not mention anything unusual as to the behavior of the phonon part of the thermal conductivity,  $\kappa_{\text{ph}}(T)$ , of these materials. They exhibit only a non-typical temperature dependence and the magnitude of the Lorentz number which influences the electronic part of the thermal conductivity  $\kappa_e(T)$ .

Materials with static MV behave as usual classic crystalline materials and do not reveal any features in  $\kappa_{\text{ph}}(T)$  and  $\kappa_e(T)$  associated with the MV of their RE ions.

As concerns the materials with the inhomogeneous MV there are practically no publications on their thermal conductivity. The present work is devoted to a representative of such materials, namely,  $\text{Sm}_3\text{S}_4$ . The thermal conductivity serves in this case, as usual, as a sensitive probe detecting phonon and electron interactions.

## 2. EXPERIMENTAL

The polycrystalline  $\text{Sm}_3\text{S}_4$  sample was prepared by rf melting in a tantalum crucible that was placed in a sealed molybdenum container. Preparation details are described elsewhere [4]. X-ray diffraction analysis showed the sample to be single-phase with a well-defined  $\text{Th}_3\text{P}_4$  cubic



**Fig. 1.** (a) Dependence of the lattice constant of  $\text{Sm}_x\text{S}_4$  ( $\text{Sm}_x\text{S}_{1.333}$ ) on  $x$  [5]. The  $a = 8.505$  Å value corresponds to the sample studied, (b) Temperature dependence of  $\kappa_{\text{tot}} = \kappa_{\text{ph}}$  of  $\text{Sm}_{0.995}\text{S}_{1.333}$ .

structure and a lattice constant  $a = 0.8505$  nm. According to Ref. 5, this value of  $a$  corresponds not to the stoichiometric formula  $\text{Sm}_3\text{S}_4$  ( $\text{Sm}_{1.333}$ ) but rather to a composition shifted slightly toward  $\text{Sm}_2\text{S}_3$  which may be approximated as  $\text{Sm}_{0.995}\text{S}_{1.333}$  (Fig. 1a). The divalent ( $\text{Sm}^{2+}$ ) and trivalent ( $\text{Sm}^{3+}$ ) samarium ions are statistically distributed over the equivalent lattice sites in a 1:2 ratio. Thus, the sample may be described as  $\text{Sm}^{2+}\text{Sm}_2^{3+}\text{S}_4^{2-}$ .

The thermal conductivity was measured using the stationary heat flux method in the broad temperature range 4 to 300 K. The sample chamber temperature was stabilized to within an accuracy of better than  $\pm 3 \times 10^{-3}$  K. The sample temperature and temperature gradient along the sample were measured by a constantan-Manganin thermocouple. The temperature gradient along the sample was in the range 0.1 to 0.5 K. Particular care was taken to avoid parasitic heat transfer between the sample and its environment. The sample was placed inside the cylindrical screen. The temperature of the screen was electronically stabilized at the level of the sample. All current and voltage leads were thermally anchored to the screen. The measurement error was below 2%, and the surplus error estimated from the scatter in the measurement points, did not exceed 0.3%. The electrical resistivity of the samples was measured [3] by the standard four-probe method to an uncertainty of about 3%. The experimental setup and the measurement procedure have been described in detail in Ref. 6.

### 3. RESULTS AND DISCUSSION

$\text{Sm}_3\text{S}_4$  is an  $n$ -type semiconductor with a fairly high electrical resistivity [3], which decreases exponentially with temperature. The activation

energy for a hopping mechanism equal to 0.13 eV agrees with a value reported for stoichiometric samples of  $\text{Sm}_3\text{S}_4$  [2, 3]. According to the Wiedemann–Franz relation, the electronic contribution to thermal conductivity does not exceed  $0.0255 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ , which is less than 2% of the measured thermal conductivity  $\kappa_{\text{tot}}$  (Fig. 1b). Thus, a measured thermal conductivity is composed almost entirely of the phonon contribution. The temperature variation of the thermal conductivity of  $\text{Sm}_{0.995}\text{S}_{1.333}$  plotted in Fig. 1b exhibits a pronounced maximum at 25 K, which is usually observed in semiconductors [7]. Then, the thermal conductivity diminishes when the temperature is raised to 300 K. This temperature variation in the range 30

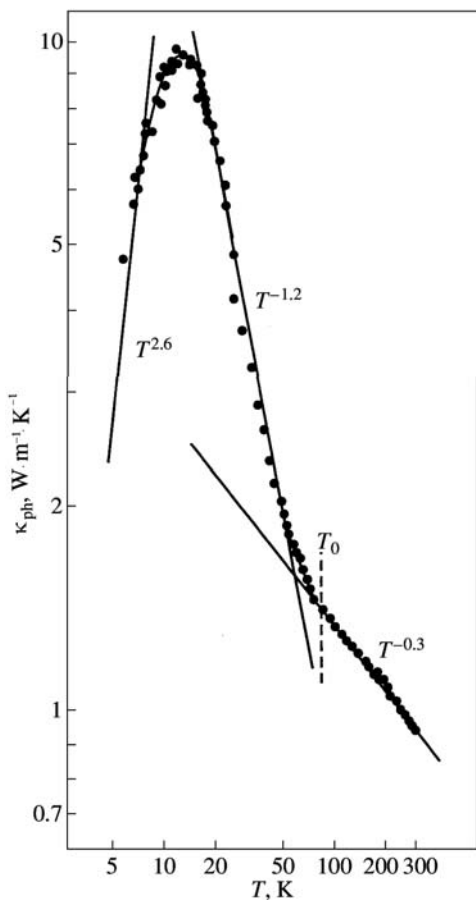


Fig. 2. Temperature dependence of  $\kappa_{\text{ph}}$  for the  $\text{Sm}_{0.995}\text{S}_{1.333}$  sample studied.

to 80 K agrees reasonably well with our earlier measurements of thermal conductivity in the stoichiometric compound  $\text{Sm}_3\text{S}_4$  [8].

Several intervals can be distinguished in a double logarithmic plot of thermal conductivity variation with temperature (Fig. 2). Such a plot can be used to calculate exponents in relations like  $\kappa \sim T^n$  with an uncertainty of 0.05. In the low temperature interval below a maximum in  $\kappa(T)$ , the thermal conductivity may be approximated as  $\kappa \sim T^{2.6}$ . Such a variation is typical for most crystalline materials. Above the maximum in the interval from 20 to 50 K, the thermal conductivity varies as  $\sim T^{-1.2}$ . This behavior is characteristic for sufficiently perfect solids, for which theory suggests  $n = -1$ . Above  $T_0 = 95$  K, the exponent of thermal conductivity switches to  $n = -0.3$ , which is characteristic of heavily defected materials. This changeover reveals a new phonon scattering mechanism coming into play. In order to analyze this changeover in detail, the measured thermal resistivity  $W_{\text{ph}} = \kappa_{\text{ph}}^{-1}$  was plotted in Fig. 3. In the inset the schematic temperature

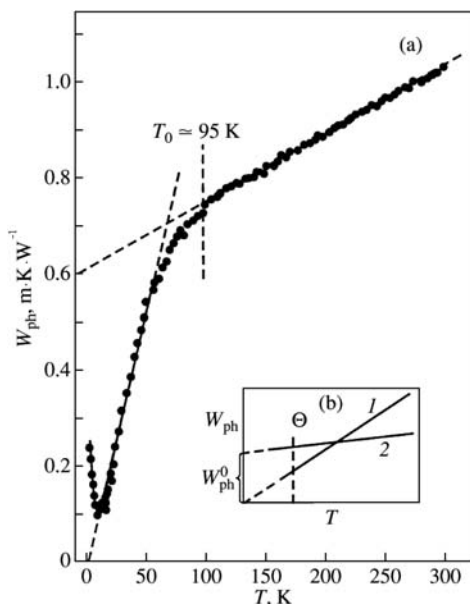


Fig. 3. (a) Temperature dependence of the lattice thermal resistivity ( $W_{\text{ph}} = 1/\kappa_{\text{ph}}$ ) of the  $\text{Sm}_{0.995}\text{S}_{1.333}$  sample studied, and (b) schematic of the temperature dependence of thermal resistivity of (1) a defect-free sample and (2) a sample with defects.  $W_{\text{ph}}^0$  is the residual thermal resistivity for a defect sample, and  $\Theta$  is the Debye temperature.

variation of thermal resistivity was plotted for the defected and defect-free samples. It is well known that the residual thermal resistivity of perfect solids should be zero, whereas the defected materials exhibit a relatively high residual thermal resistivity (Fig. 3b). A comparison of the measured thermal resistivity of the  $\text{Sm}_{0.995}\text{S}_{1.333}$  sample in the inset shows that above  $T_0$  the additional phonon scattering mechanism appears. The most plausible explanation suggests that electron hopping from  $\text{Sm}^{2+}$  to  $\text{Sm}^{3+}$  in compounds with inhomogeneous MV, to which  $\text{Sm}_3\text{S}_4$  belongs, generates local stresses in the lattice, resulting in a change of the temperature dependence from  $\kappa \sim T^{-1.2}$  to  $\kappa \sim T^{-0.3}$  and in an appreciable thermal resistivity. A simple picture is based on the fact that the ionic radius of  $\text{Sm}^{2+}$  is considerably larger than that of  $\text{Sm}^{3+}$ . Thus, the electron hopping from  $\text{Sm}^{2+}$  to  $\text{Sm}^{3+}$  changes their ionic radii, and this results in a local lattice rearrangement generating stresses (compressive and tensile) around these ions. The lattice is breathing and cannot apparently relax completely in one electron hopping cycle. The local stresses thus created possibly act as additional phonon scattering centers responsible for the noticeable thermal resistivity.

#### 4. CONCLUSION

The thermal conductivity and the electrical resistivity of mixed-valance compound  $\text{Sm}_3\text{S}_4$  was measured in the range 4 to 300 K. The electron hopping from  $\text{Sm}^{+2}$  to  $\text{Sm}^{+3}$  in compounds with inhomogeneous MV, to which  $\text{Sm}_3\text{S}_4$  belongs, generates local strains in the lattice, resulting in a change of the temperature dependence from  $\kappa_{\text{ph}} \sim T^{-1.2}$  to  $\kappa_{\text{ph}} \sim T^{-0.3}$  and in an appreciable thermal resistivity.

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