

Thermal properties of  $\text{Eu}_3\text{S}_4$ : Order-disorder transition

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Capacitive thermal-expansion, specific-heat, and electrical-resistivity measurements on single crystals of  $\text{Eu}_3\text{S}_4$  and  $\text{La}_3\text{S}_4$  have established for  $\text{Eu}_3\text{S}_4$  a first-order, nonstructural phase transition near  $T_i=186$  K and the entropy change  $\Delta S=9\pm 0.9$  J/mole K of an order-disorder transition with a configurational entropy  $R \ln 3$ . The transition exhibits  $\Delta V/V=9\times 10^{-4}$  and  $d \ln T_i/dp=d \ln E_a/dp=-8.7\times 10^{-11}$  Pa $^{-1}$ , i.e., a proportionality between  $T_i$  and the activation energy  $E_a$  of the resistivity.

Homogeneous mixed-valence compounds have attracted much attention in recent years because of valence fluctuations, which in the inhomogeneous mixed-valence counterpart are due to thermally activated hopping between equivalent cation sites.<sup>1</sup> In the latter class of materials the basic questions concerning charge ordering at low temperatures, associated lattice distortions, and order-disorder phase transitions have not been answered unambiguously to date.<sup>2,3</sup> The reason lies in the rather poor, ambiguous experimental evidence, obscured mainly by inherent problems in sample preparation, stoichiometry, and purity.<sup>3</sup> On the other hand, a clear statement about a charge-ordered state in inhomogeneous mixed-valence systems and about the magnitude of the associated lattice distortion could help to clarify questions concerning intersite couplings<sup>4</sup> in homogeneous mixed-valence systems: lowering of the ground-state energy due to charge fluctuations,<sup>5</sup> or spatial correlations of rare-earth ions,<sup>6</sup> Wigner lattice formation,<sup>7</sup> and qualitative changes in Fermi surface.<sup>8</sup>

The prominent inhomogeneous mixed-valence compound  $\text{Eu}_3\text{S}_4$  with equivalent Eu sites at room temperature, but inequivalent  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  sites at low temperature,<sup>9</sup> represents an ideal test case because of the well-defined change in configurational entropy for a complete order-disorder transition.<sup>10</sup> However, the small entropy change observed<sup>10</sup> as well as the lack of conclusive evidence from x-ray

data about structural changes at the phase transition near 175 K (Ref. 11) did not support the previously suggested ( $\text{Eu}^{2+}$ - $\text{Eu}^{3+}$ ) charge order-disorder transition.<sup>12</sup> Hence the nature of the phase transition near 175 K (Refs. 11 and 13) or 160 K (Ref. 10) and the question concerning charge ordering at low temperature are still undetermined particularly due to problems with sample stoichiometry.<sup>3</sup>

We report on measurements of (capacitive) thermal expansion, specific heat, and electrical resistivity for the first time on *single crystals* of  $\text{Eu}_3\text{S}_4$  compared with those of  $\text{La}_3\text{S}_4$ . Hence we show for the first time that the phase transition of  $\text{Eu}_3\text{S}_4$  near  $T_i=186$  K is of *first order*, exhibiting the configurational entropy of an *order-disorder* transition and that the values of  $T_i$  and of the activation energy  $E_a$  of the resistivity for  $T < T_i$  ( $E_a=0.32$  eV) are proportional ( $E_a \sim T_i$ ). The structural contribution to the phase transition of  $\text{Eu}_3\text{S}_4$  is found to be very small compared to the second-order (structural) phase transition of  $\text{La}_3\text{S}_4$ .

The relative length change  $\Delta L/L$  has been measured by a capacitive method<sup>14</sup> between 1.5 and 380 K (sensitivity  $10^{-7}$ , accuracy  $\pm 2\%$ ). This very sensitive method could be applied for the first time in the temperature range around  $T_i$ , which is usually not easily accessible. The linear thermal-expansion coefficient  $\alpha$  has been calculated by a spline fit to  $\Delta L/L$  (Ref. 15) (sensitivity  $10^{-8}$  K $^{-1}$ , accuracy  $\pm 2\%$ ). The specific heat  $C_p$  ( $20 < T < 350$

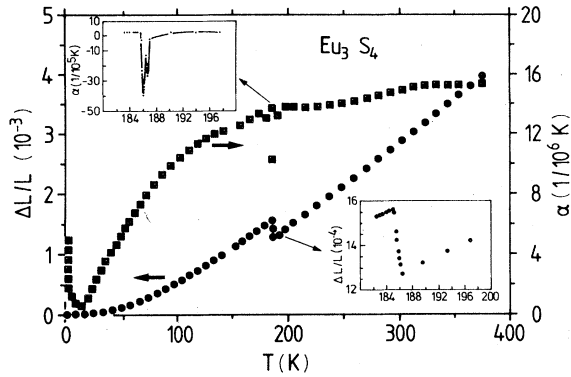


FIG. 1. Relative length change  $\Delta L/L$  and linear thermal-expansion coefficient  $\alpha$  of  $\text{Eu}_3\text{S}_4$  single crystal (unoriented) as function of temperature.

K) has been measured by a calorimeter described elsewhere<sup>16</sup> (accuracy  $\pm 2\%$ ). The preparation of the single crystals of  $\text{La}_3\text{S}_4$  and  $\text{Eu}_3\text{S}_4$  with lattice parameters  $a = 8.724 \pm 0.001$  Å and  $a = 8.532 \pm 0.001$  Å at 300 K, respectively, is described elsewhere.<sup>17,18</sup>

In Fig. 1 we show  $\Delta L/L$  of the unoriented  $\text{Eu}_3\text{S}_4$  single crystal (length 5.63 mm) between 1.5 and 380 K. There is a sharp discontinuity at  $T_t = 186$  K.  $\alpha$  shows a monotonic continuation above and below  $T_t$ . The anomaly in  $\alpha$  near  $T = 3.8$  K is attributed to the ferromagnetic ordering of  $\text{Eu}_3\text{S}_4$ .<sup>10</sup> The jump in  $\Delta L/L$  [inset of Fig. 1 (bottom)] with increasing temperature is  $-3 \times 10^{-4}$  with a width of only about 1 K.

Figure 2 shows  $\Delta L/L$  and  $\alpha$  of the unoriented single crystal (length 6.04 mm) of  $\text{La}_3\text{S}_4$ . Contrary to  $\text{Eu}_3\text{S}_4$ ,  $\Delta L/L$  is a continuous function of temperature near the structural phase transition<sup>19,20</sup> ( $T_m = 102$  K) and  $\alpha$  is not monotonically continued

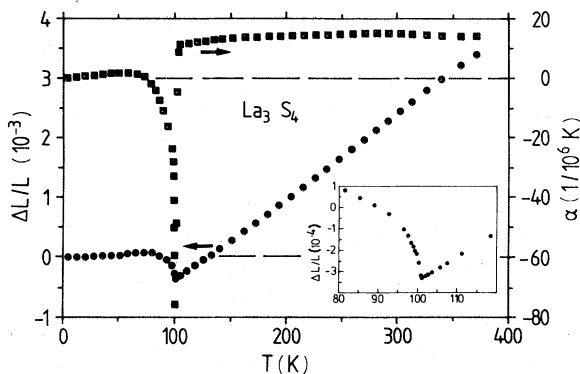


FIG. 2. Relative length change  $\Delta L/L$  and linear thermal-expansion coefficient  $\alpha$  of  $\text{La}_3\text{S}_4$  single crystal (unoriented) as function of temperature.

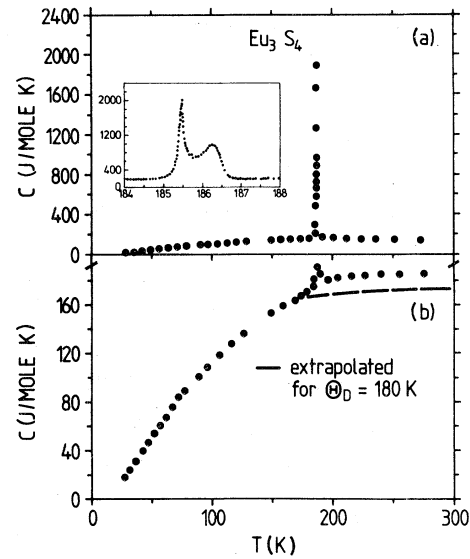


FIG. 3. Specific heat  $C_p$  of  $\text{Eu}_3\text{S}_4$  single crystal as function of temperature of full (a) and expanded (b) scale. Dashed line in (b) is the Debye fit extrapolated for  $T > 186$  K.

below and above  $T_m$ .

The specific heat of the  $\text{Eu}_3\text{S}_4$  single crystal (weight 0.4932 g) exhibits a giant anomaly [Fig. 3(a)] near 186 K. The inset of Fig. 3(a) shows a well-pronounced double-peaked structure near 185.5 and 186.3 K with an overall width of only about 1 K. Note the similarity in  $C_p$  and  $\alpha$  [see inset of Fig. 1 (top)]. No significant hysteresis could be detected, contrary to the 5-K hysteresis reported by Davis *et al.*<sup>11</sup> The entropy of the anomaly is about  $\Delta S_1 = 5.2 \pm 0.1$  J/mole K. As can be seen in Fig. 3(b) there is a step in  $C_p$  of  $\text{Eu}_3\text{S}_4$  for  $T > T_t$ . Unfortunately, for the determination of the background we cannot consider  $C_p$  of  $\text{La}_3\text{S}_4$ , since the phonon spectra of this superconductor and the mixed-valent  $\text{Eu}_3\text{S}_4$  seem to be very different. Therefore, in order to use the Debye formula as a reasonable background approximation for  $T > T_t$ , we have calculated  $C_V$  of  $\text{Eu}_3\text{S}_4$  using  $C_V = C_p - 9TV\alpha^2 B$  [ $B = 92$  GPa (Ref. 21)]. The asymptotic limit near  $T_t$  of the strongly temperature-dependent  $\Theta_D(T)$  is  $\Theta_D = 180$  K, which has been used in the above Debye fit (dashed line). The corresponding excess entropy for  $T_t < T < 400$  K is about  $\Delta S_2 = 3.8 \pm 0.8$  J/mole K. The error is mainly due to the uncertainty in  $\Theta_D$  and accounts also for the uncertainties in the extrapolation  $\Delta C_V/T \rightarrow 0$  near 400 K. Hence the total entropy is  $\Delta S = \Delta S_1 + \Delta S_2 = 9 \pm 0.9$  J/mole K.

We have also measured  $C_p$  of several agglomerat-

ed single crystals (0.5–1 mm in diameter) of  $\text{Eu}_3\text{S}_4$  prepared by the same method. They show one or two peaks with  $183.0 < T_t < 188.3$  K. The steplike behavior of  $C_p$  is also observed with similar  $\Delta S_1$  and  $\Delta S_2$  contributions as above. The width of the  $C_p$  anomaly decreases with increasing  $T_t$  towards about 1 K. Note that only  $C_p$  shows a variation in  $T_t$ , whereas the lattice parameter of all samples is  $a = 8.532 \pm 0.001$  Å. Hence  $C_p$  is a much more sensitive probe to determine the quality of a  $\text{Eu}_3\text{S}_4$  sample than the lattice parameter.

The specific heat of the  $\text{La}_3\text{S}_4$  single crystal (weight, 0.6027 g) shows a sawtooth-shaped anomaly near  $T_m = 102$  K (Fig. 4), exhibiting an entropy of about 0.9 J/mole K. This value should be taken with caution, since the phase transition is of second order (see below).

The specific electrical resistivity  $\rho$  of our semi-conducting  $\text{Eu}_3\text{S}_4$  single crystal (Fig. 5) shows a discontinuity near  $T_t = 186$  K without any significant hysteresis. With decreasing temperature,  $\rho$  increases at  $T_t$  by about a factor of 50. The activation energy  $E_a$  is  $0.32 \pm 0.01$  eV below and  $0.16 \pm 0.005$  eV above  $T_t$ .

The discontinuity of  $\Delta L/L$  of  $\text{Eu}_3\text{S}_4$  near 186 K (Fig. 1) shows for the first time that the phase transition is definitely of first order. This could not be seen by previous x-ray studies showing a rather poorly resolved transition with peak broadening and loss of intensity upon cooling through the phase transition.<sup>11</sup> On the other hand,  $\text{La}_3\text{S}_4$  does not show such a discontinuity in  $\Delta L/L$  (Fig. 2), i.e., the structural phase transition of  $\text{La}_3\text{S}_4$  is of second order, contrary to the conclusions in the literature.<sup>20,21</sup>

The linear thermal-expansion coefficient  $\alpha$  of our unoriented single crystal of  $\text{La}_3\text{S}_4$  exhibits a steplike behavior for temperatures below and above  $T_m$ .<sup>22</sup> Since  $\alpha$  of  $\text{Eu}_3\text{S}_4$  shows a uniform continuity be-

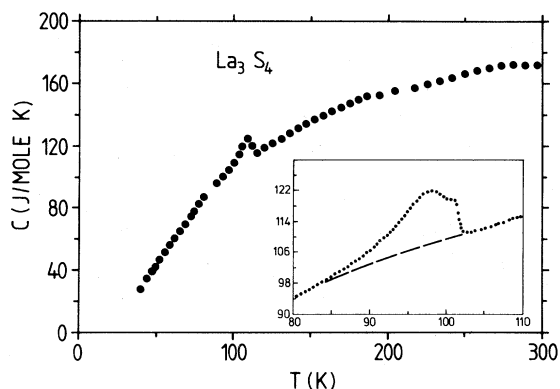


FIG. 4. Specific heat  $C_p$  of  $\text{La}_3\text{S}_4$  single crystal as function of temperature.

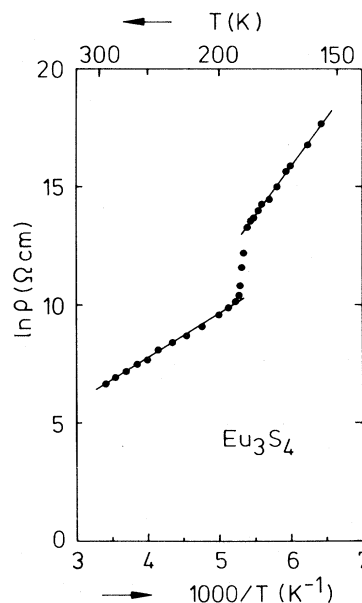


FIG. 5. Specific electrical resistivity  $\rho$  of  $\text{Eu}_3\text{S}_4$  single crystal as function of temperature.

tween 4 and 400 K, except for the peak at  $T_t$  (see Fig. 1), the phase transition of  $\text{Eu}_3\text{S}_4$  is not dominantly a structural one, i.e., there is no significant displacive effect on the Eu and S positions. This is consistent with x-ray<sup>11</sup> and recent neutron-diffraction measurements,<sup>23</sup> which show that the change of the atom positions is extremely small, indicated by a small, probably orthorhombic, distortion<sup>23</sup> for  $T < T_t$ .

From our above results we can calculate the pressure dependence of  $T_t$  of  $\text{Eu}_3\text{S}_4$  using the Clausius-Clapeyron equation  $dT_t/dp = \Delta V/\Delta S$ .  $\Delta S$  and  $\Delta V$  are the entropy and the volume change, respectively, at the phase transition. With  $\Delta S = 5.2$  J/mole K we obtain  $dT_t/dp = -(1.6 \pm 0.1) \times 10^{-8}$  K/Pa, i.e., we predict that  $T_t$  decreases with increasing pressure. In contrast to  $\text{Eu}_3\text{S}_4$ ,  $\text{La}_3\text{S}_4$  is known to have a positive pressure coefficient  $dT_m/dp = +(1.6 \pm 0.15) \times 10^{-8}$  K/Pa.<sup>24</sup>

The measured total entropy  $\Delta S = 9$  J/mole K equals about  $R \ln 3$ . The configurational entropy of an order-disorder transition where three configurations (one  $\text{Eu}^{2+}$  and two  $\text{Eu}^{3+}$ ) are involved in  $R \ln 3$ .<sup>10</sup> Hence the *first-order* transition of  $\text{Eu}_3\text{S}_4$  is of *order-disorder* type. Note that our entropy is a factor of 3 times larger than the value reported previously.<sup>10</sup> We attribute this difference to our better sample quality reflected by  $T_t = 186$  K compared to 160 K,<sup>10</sup> a width of the  $C_p$  anomaly of 1 K compared to 7 K,<sup>10</sup> and a lattice parameter of  $a = 8.532$  Å compared to 8.507 Å.<sup>10</sup> Furthermore, the entrop-

py of the  $C_p$  anomaly of  $\text{La}_3\text{S}_4$  is 10 times smaller than that of  $\text{Eu}_3\text{S}_4$ , indicating again the different nature of the phase transition (second order, structural,  $dT_m/dp > 0$ ) of  $\text{La}_3\text{S}_4$  compared to  $\text{Eu}_3\text{S}_4$  (first order,  $dT_t/dp < 0$ ).

The steplike behavior of  $C_p$  of  $\text{Eu}_3\text{S}_4$  for  $T > T_t$  [see Fig. 3(b)] is assumed to be a short-range-order effect, extending roughly up to 400 K. Such a contribution was predicted in mean-field theory.<sup>25</sup> However, the reported sign is different. A similar double-peaked structure like that of the  $C_p$  anomaly of  $\text{Eu}_3\text{S}_4$  [inset Fig. 3(a)] has also been observed in  $\text{Fe}_3\text{O}_4$  and has been attributed to residual strain effects.<sup>26</sup> The number of peaks, their positions and relative widths depend on the thermal treatment of  $\text{Fe}_3\text{O}_4$ . While this possibility cannot be ruled out completely for  $\text{Eu}_3\text{S}_4$ , temperature cycling between 4 and 400 K did not show any significant change in position, width, and height of the  $C_p$  anomaly. Another explanation of the double-peaked structure of  $C_p$  and of  $\alpha$  of  $\text{Eu}_3\text{S}_4$  could be a certain inhomogeneity of our single crystal, showing up in two slightly different transition temperatures within 1 K. We would like to mention that  $C_p$  of some of our agglomerated single crystals show only a single-peaked anomaly with a maximum  $T_t$  of 188.3 K (width about 1 K,  $\Delta S_1 = 5.6$  J/mole K).

The activation energy of  $\rho$  of our  $\text{Eu}_3\text{S}_4$  single crystal ( $E_a = 0.16$  eV) for  $T > T_t$  is the same as all values published so far<sup>9,13</sup> and appears to be an intrinsic property. On the other hand, the magnitude of  $E_a$  for  $T < T_t$  seems to be correlated with that of  $T_t$ , amounting to  $E_a = 0.32$  eV,  $T_t = 186$  K for our single crystal as compared to  $E_a = 0.21$  eV,  $T_t = 175$  K reported in the literature.<sup>13</sup> Assuming a proportionality between  $E_a$  and  $T_t$  we obtain  $d \ln T_t / dp = d \ln E_a / dp = -8.7 \times 10^{-11}$  Pa<sup>-1</sup>,

which is in excellent agreement with the pressure coefficient of  $E_a$  found in Mössbauer spectroscopy.<sup>27</sup> Such a proportionality  $E_a \sim T_t$  has been found in  $\text{Fe}_3\text{O}_4$  (Ref. 28) and is suggestive of a Mott-Wigner transition in  $\text{Eu}_3\text{S}_4$  as well. This is consistent with the charge ordering and with the drop in carrier concentration by roughly 3 orders of magnitude<sup>29</sup> upon cooling below  $T_t$ .

The electrical resistivity of  $\text{Eu}_3\text{S}_4$  may also be due to a polaron hopping process.<sup>13</sup> The activation energy  $E_{a,\text{pol}}$  associated with this process can be assumed as proportional to  $1/\omega_0^2$ , where  $\omega_0$  is an optical-phonon frequency.<sup>30</sup> By using the Grüneisen formula we obtain  $d \ln E_{a,\text{pol}} / dp = -2d \ln \omega_0 / dp = 6\alpha V / C_V = -4.8 \times 10^{-11}$  Pa<sup>-1</sup>, which again is in reasonable agreement with  $d \ln E_a / dp$ .<sup>27</sup>

We would like to emphasize that our results reveal a very strong similarity between  $\text{Eu}_3\text{S}_4$  and  $\text{Fe}_3\text{O}_4$ , concerning first-order phase transitions near  $T_t$  and  $T_V$  (Verwey temperature) and associated entropy ( $\Delta S = \Delta S_1 + \Delta S_2$ ), volume and resistivity changes, pressure coefficients of  $T_t$  and  $T_V$ , and absence of thermal hysteresis.

*Note added in proof.* The predicted sign and magnitude of  $dT_t/dp$  has recently been confirmed by electrical resistivity measurements under pressure.<sup>31</sup>

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