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SPECIFIC HEAT AND TRANSPORT PROPERTIES OF $SmIn_3$

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The specific heat of polycrystalline $SmIn_3$ has been measured over the temperature range of 0.5 K to 25 K. At 15.2 K it revealed a λ–type anomaly which was associated with the antiferromagnetic (AFM) phase transition. Below 11 K the specific heat showed the usual temperature dependence expressed by the formula $Cp = \gamma T + \delta T^3$, the last term being the sum of the lattice (βT^3) and the magnetic (αT^3) specific heats. The entropy related to the transition was close to the value $S = R \ln 4$, which was expected for the lowest laying crystalline field quartet. The thermal and electrical conductivity of $SmIn_3$ (polycrystal), as well as of polycrystalline samples of $LaIn_3$ was measured in the temperature range between 4 K and 40 K. The crystal–field Lorenz number was calculated from the magnetic contributions to the thermal and electrical conductivity. It turned out to be a decreasing function of temperature as a result of different effects of inelastic scattering on the thermal and electrical kinetic coefficients.

Key words: $SmIn_3$, specific heat, crystalline field, kinetic coefficients.

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I. SPECIFIC HEAT

The intermetallic compound $SmIn_3$ crystallizes in a primitive cubic structure of the $AuCu_3$–type. It becomes antiferromagnetically ordered below 16 K [1]. In this paper measurements of the specific heat of $SmIn_3$between 0.5 K and 25 K are reported.

The measurements were carried out by an adiabatic method in the apparatus described elsewhere [2]. The sample was prepared by arc melting the components on water–cooled copper base in a pure–argon atmosphere. The starting materials were 3N pure Samarium and 5N pure Indium. The quality and phase homogeneity were confirmed by an X–ray diffraction.

The specific heat of $SmIn_3$ (Fig. 1) revealed a λ–type anomaly due to the AFM ordering below $T_N = 15.2$ K. From the susceptibility measurements some higher Neel temperature, $T_N = 16$ K was reported by Buschow et al. [1].

In addition to the usual lattice and electronic terms, the magnetic specific heat due to exchange interactions between the electronic spins also contributed in the temperature range where the measurements were done. At the temperatures below 1 K a nuclear specific heat of Sm ions is also significant [3].

In order to extract the magnetic contribution C_M to the specific heat, we had assumed that the lattice (C_L) and the electronic (C_E) terms for $SmIn_3$ were the same as for $LaIn_3$, as given by Nasu et al. [4] and Van Diepen et al. [5].

After the substraction of the $LaIn_3$ heat capacity from that measured for $SmIn_3$ we can give an estimate for the entropy related to the phase transition. Presumably, the short range ordering which still causes an extra contribution above the Neel point, does not contribute significantly above 25 K. The entropy related to the transition was equal to 10.9 J/mole. This was close to the value $S = R \ln 4 = 11.5$ J/mole which was expected for the lowest laying crystalline electric field (CEF) quartet (effective spin 3/2). The entropy change above T_N amounts to 30 % of $R1n4$.

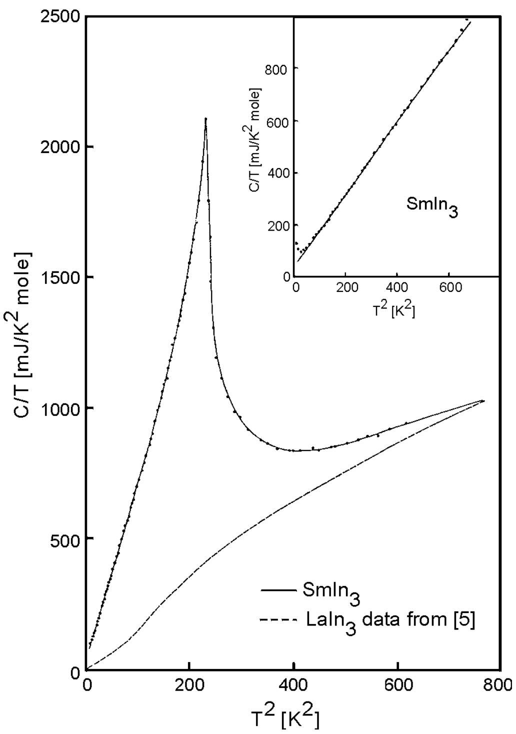

Fig. 1. The specific heat of $SmIn_3$ against temperature around the antiferromagnetic phase transition as well as in the lower temperature range (insert). $LaIn_3$ specific heat data are also shown [5].

The best agreement with the data was obtained with C_M proportional to $T^{2.7}$. The magnetic specific heat as function of temperature was plotted in Fig. 2. The straight line corresponds to the equation $C_M = 10.8T^{2.7}$ mJ/K mole. Kimura [6] has shown that a different kind of dependence, besides the expected T^3 dependence may occur in the case of a strong magnon–phonon coupling in an antiferromagnet.

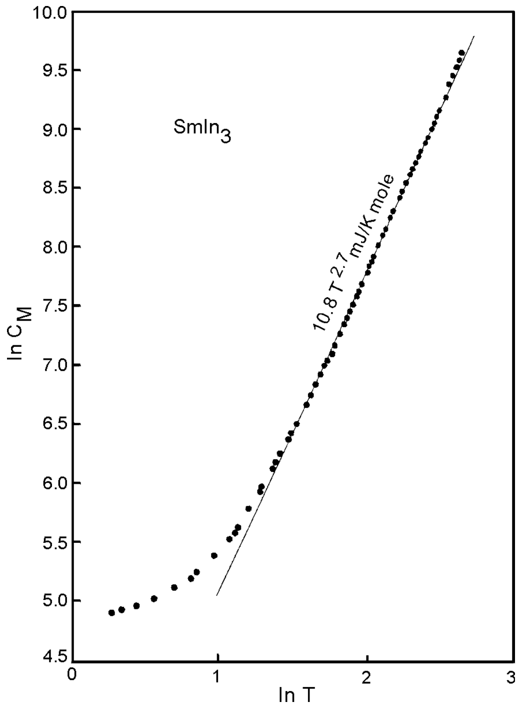

Fig. 2. Magnetic contribution to the specific heat of $SmIn_3$ against the temperature, as extracted from the measuring of specific heat and the electronic part and the lattice contribution of Lam_3.

On Fig. 1 the commonly used Cp/T vs T^2 plot is also shown. Below 11 K the data appeared to be represented in a satisfactory fassion by the formula $Cp = \gamma T + \delta T^3$ where the first term corresponded to the electronic contribution and the second term was the sum of the lattice and the magnetic specific heats. The values of the constants were (for specific heat in mJ/K mole) $\gamma = 42$ and $\delta = 4.65$. The electronic specific heat coefficient γ determined in this manner was very high in comparison with the values of 6.3 for $LaIn_3$ [4] and 11.4 for $PrIn_3$ [4] respectively. Assuming the lattice contribution to be the same as for that of $LaIn_3$, we can present the magnetic contribution to the specific heat as $C_M = 3.59T^3$ mJ/K mole.

Below 4 K an anomaly in the specific heat was observed, most probably due to Sm^{3+} as magnetic "impurities". We think that the temperature dependence of the difference $C_{imp} = Cp - 42T - 4.65T^3 - C_N$ (here for C_N we have adopted the value given by Lounasmaa [3] for the nuclear specific heat of Samarium metal) with the maximum at 1.35 K (Fig. 3) is characteristic for magnetically ordered Sm^{3+} ions in $SmIn_3$. The entropy associated with these "impurities" equaled $S = 233$ mJ/K mole which means that only 1.57 % Sm^{3+} ions are bounded to $SmIn_3$. It is difficult to decide what was the real temperature dependence of C_M. The T^3 — temperature dependence implies to large value of the electronic specific heat. A decision about it could give specific heat measurements in high magnetic fields, of the same order of magnitude as T_N (on the energy scale).

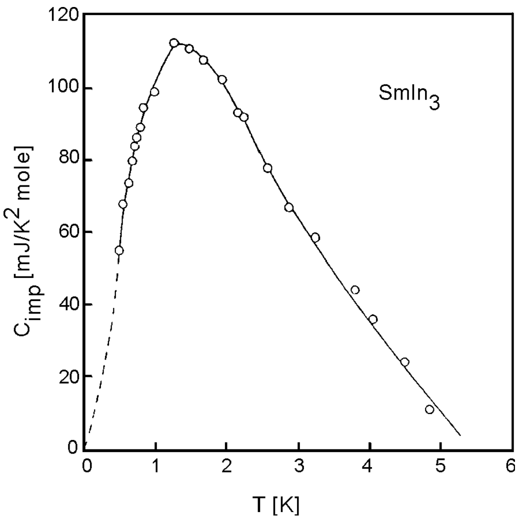

Fig. 3. Temperature dependence of the excess part of the specific heat of SmIn over the electronic, lattice, and hyperfine specific heat. See the text.

II. TRANSPORT PROPERTIES

Recently, there has been considerable interest in the effects of CEF on the electron transport properties of rare–earth intermetallic compounds as metallic systems containing magnetic ions [7–9]. $SmIn_3$ is one of the intermetallic compounds just in this category. In such compounds the scattering cross–section for conducting electrons depends upon the temperature as a consequence of the CEF splitting of the $4f$–electron level of the rare–earth ions [10,11]. Therefore, studies of the transport properties provide information of the CEF level scheme of the rare–earth ion, and also of the scattering mechanisms. Among the intermetallic compounds of rare–earths, compounds where the CEF ground state is a singlet are particularly interesting because fairly large CEF effects are expected to be seen in transport properties at low temperatures.

An additional fact which in some sense may complicate the physical picture in $SmIn_3$ is that the Sm valence may be different, the ratio Sm^{3+}: Sm^{2+} (i.e. $4f^6$ to $4f^5$ electron configuration) not being well established. The change of the Sm valence should be somehow correlated with the transport properties. We present here the results of thermal conductivity and electrical resistivity measurements of $SmIn_3$ in the temperature range from 4 K to 40 K, together with the results on $LaIn_3$, as a non–magnetic counterpart of $SmIn_3$, which does not possess 4f electrons and a magnetic moment, as well. The measurements of $LaIn_3$ which are isomorphous with $SmIn_3$ suggested that the thermal conductivity in the last compound should be governed by conduction electrons. All these measurements definitely showed the effect of CEF. By comparing the temperature dependence of the thermal conductivity of $SmIn_3$ with the theory of CEF effects and heat transfer phenomena, the energy separation between the ground and the first exited states may be determined and compared with the known CEF level scheme.

The thermal conductivity λ (T) was measured at the temperatures between 4 K and 40 K by the standard steady state method [12]. One end of the sample was soldered to a copper holder which was a part of the copper heat sink. Heat was supplied to the sample by a Constantan heater fastened to the other end by GE 7031 varnish and the temperature gradient across the sample was measured by two Allen Bradley carbon thermometers glued to it with the accuracy of about 1mK. These thermometers were calibrated against a manufacturer calibrated Lake Shore carbon–glass thermometer attached to the cold end of the sample. The temperature gradient was usually 0.02 to 0.3 K/cm depending upon the temperature of measurement. The thermal conductivity was obtained by computer fit from the data of the heater power, the temperature gradient and the geometry of the sample. The error was estimated to be less than 5 %, mainly due to geometrical inexactnesses.

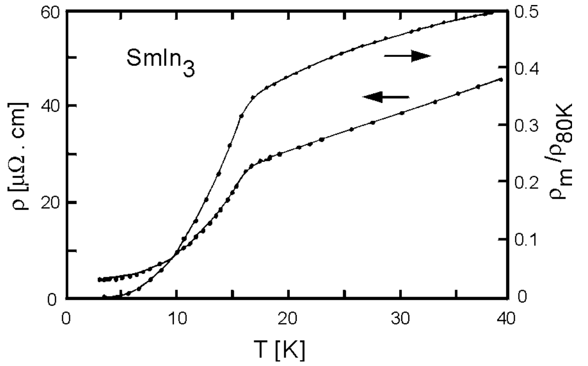

Fig. 4. Electrical resistivity and relative magnetic part $\rho_m/\rho(\mathrm{T}{=}80\ K)$.

The electrical resistivity was measured by the conventional four–terminal AC techniques using a precision Princeton Applied Research Model 5302 Lock–in Amplifier. An extended range low–temperature addenda to a standard Gifford–McMahon two–stage cryogenerator was used to produce temperatures between 4 K and 40 K. The sample for measuring of thermal and electrical conductivity was cut as an elongated bar of the dimension of 40x2x2 mm^3 from the same poly–crystalline $SmIn_3$ rod on which the specific heat has been measured. Fig. 4 displays the absolute electrical resistivity of $SmIn_3$ and the magnetic contribution obtained by extracting the $LaIn_3$ resistivity and normalized to the resistivity at 80 K. The CEF effects are clearly evidenced as well as a dramatic anomaly at T_N.

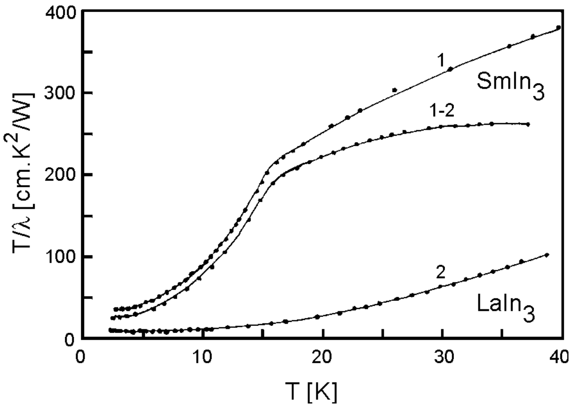

Fig. 5. Thermal resistivity multiplied by the temperature (T/λ) of $SmIn_3$ and $LaIn_3$ vs. temperature. The "1–2" curve is the magnetic part of thermal resistivity of $SmIn_3$.

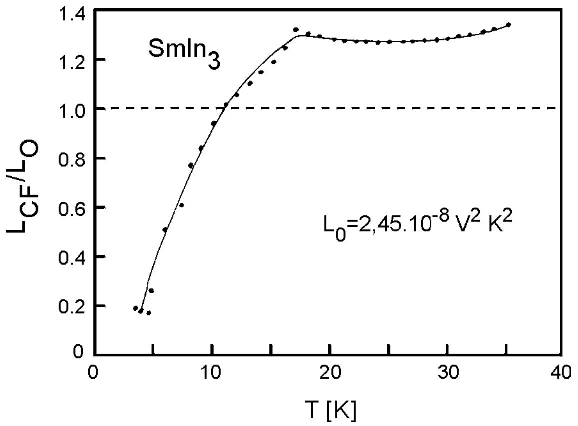

Fig. 6. Temperature dependence of the CEF Lorenz number for $SmIn_3$

The results of the same procedure are presented at Fig. 5 where the thermal resistivity $W(1/\lambda)$ is shown as multiplied by T. In this way all other contributions such as those from impurity or electron–phonon scattering are separated from the "magnetic" part of resistivities due to CEF effects.

As the thermal conductivity of metals is governed by the electron electrical thermal conductivities are a sum of contributions from different scattering processes, according to Matthisen's rule. From the magnetic contributions to the thermal and electrical resistivities the CEF Lorenz number L_{CF} was calculated:

$$L_{CF} = \rho_{CF}/W_{CF}T. \qquad (1)$$

The data for the ratio (L_{CF}/L_O) are shown in Fig. 6. For metals where only electrons contribute to the thermal conductivity, the relative Lorenz number (L_{CF}/L_O) is equal to unity insofar as there are only elastic scattering processes [12]. Inelastic scattering processes, however, have different effects on the thermal and electrical conductivities, leading to the suppression of the Lorenz number. Qualitatively, because no elastic scattering is possible on the singlet ground state level, at low temperatures there is only inelastic scattering (transition from singlet to doublet, e.g. $\Gamma_1 - \Gamma_6$) and consequently low values of (L_{CF}/L_O) . With the increase of T the (Γ_6) doublet becomes populated, elastic scattering becomes possible and the CEF Lorenz number increases. So it seems the singlet ground state is also possible, most probably due to the Sm^{2+} ions.

The magnetic part of the thermal conductivity of $SmIn_3$ may be analyzed as follows.

The low temperature thermal conductivity of a metal may be written as [12]

$$T/\lambda(T) = \rho_r/(L + BT^3) \qquad (2)$$

where ρ_r is the residual resistivity, L is the Lorenz number and BT^3 is the term due to scattering by phonons. The temperature dependence above T_N can be interpreted in terms of the CEF splitting of the $4f$–levels in $SmIn_3$. The ${}^6H_{5/2}$ state of the Sm ion is split by the effect of CEF onto the number of levels of which the ground state may be a singlet. In such a system the Hamiltonian for the interaction of conduction electrons with the Sm ions is given by [13]:

$$\Re = Vo - \sum_{k_1k^1} 2Jex(k_1k^1)(g_J - 1)J(k)S(k^1) + \Re_Q \quad (3)$$

where the first term represents the interaction with the spherical part of the screened Coulomb charge, the second term — the exchange interaction with $4f$ spins of Sm ions and the third term the interaction with the electric quadrupole of the Sm ion. In this expression, g_J is the Landes g–factor, Jex is the $s - f$ exchange parameter. From this Hamiltonian the equation for the electronic thermal conductivity is obtained as [14]:

$$\lambda(T)/T = \int_0^\infty \frac{x}{1+\cosh x} F\,(X;T)\,dx \qquad (4)$$

with

$$F\,(X;T) = \left| Vo^2 + \sum_{ij} |< i|V|j >|^2 \,(n_i + n_j)x \frac{(1/2)(1+\cosh x)}{\cosh(\Delta_{ij}/kT) + \cosh x} \right|^2 \qquad (5)$$

where

$$n_i = \exp(E_i/kT)/\sum_j D_j \exp(-E_j/kT) \qquad (6)$$

and

$$\Delta = E_i - E_j. \qquad (7)$$

Here $|i>$ and $|j>$ are the wave functions for the i–th and j–th CEF states and D_j is the multiplicity of the state $|j>$. According to the equation $\lambda(T)/T$ depends upon temperature through a change of the population of each CEF state with temperature and also different matrix elements between the states. In order to analyze the experimental data for $\lambda(T)/T$ using these equations, we consider only two low–lying states and assume that the major contribution to the thermal conductivity comes from the matrix element between these states at low temperatures. Then, the experimental data can be fitted to eq.4 by choosing appropriate values for the two adjustable parameters, the energy separation between the ground state and the first exited state (Δ) and the matrix element between states, $(1/Vo^2| < i|V|j > |^2$, where $V = \Re - Vo$. The best fit is obtained with

$$\Delta/k_B = 28\ \mathrm{K} \pm 1\ \mathrm{K}$$

and

$$(1/Vo^2 \sum_{ij} | < i|V|j > |^2 = 2.1 \pm 0.1.$$

A temperature dependence similar to the one above should exist for the electrical conductivity, the theoretical expression being, of course, somewhat different from eq. 4.

The value 28 K for Δ is close to the value 30 K, the energy separation between the ground state (a Γ_2 doublet) and the first exited state (Γ_6 doublet) in $SmIn_3$. But it is undoubtedly clear, that more detailed studies of the CEF splitting in $SmIn_3$ are desirable to confirm the present results.

III. CONCLUSION

A. The specific heat of $SmIn_3$ reveals a l–type anomaly due to the AFM ordering below $T_N = 15.2$ K. This temperature concurs well the results of Bushow et al. [1] in magnetic susceptibility. From the experimental data on the magnetic contribution of C_M to the specific heat, we calculated that $C_M = 10.8.T2.7$ mJ/(K mole). This dependence was different from the expected $C_m \sim T^3$ [6], that may occur in the case of strong magnon–phonon coupling in an antiferromagnet. The value concurs well with the effective spin 3/2 of the lowest laying CEF quartet.

B. The change of the Sm valence correlated with the transport properties. The scattering processes during the transfer of energy and charge in the temperature interval 4–40 K are separated from the "magnetic" part of resistivities due to the CEF effects. From the magnetic contributions of the thermal and electrical resistivities the CEF Lorenz LCF number was calculated. Inelastic scattering processes have different effects on the thermal and electrical conductivities leading to a suppression of the Lorenz number.

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ПИТОМА ТЕПЛОЄМНІСТЬ ТА ВЛАСТИВОСТІ ПЕРЕНОСУ $SmIn_3$

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Виміряно питому теплоємність полікристалічного $SmIn_3$ в температурному інтервалі від 0.5 K до 25 K. При 15.2 K спостерігалась λ–подібна аномалія, яка пов'язана з антиферомагнетним (АФ) фазовим переходом. При температурі нижчий від 11 K питома теплоємність мала звичайну температурну залежність, що виражається формулою $C_p = \gamma T + \delta T^3$, де останній член — сума ґраткової (βT^3) та магнетної (αT^3) питомих теплоємностей. Пов'язана з переходом ентропія близька до величини $S = R \ln 4$, яка є сподіваною для найнижчого квартету кристалічного поля. Тепло– та електропровідність $SmIn_3$ (полікристал), а також полікристалічних зразків $LaIn_3$ вимірювалась у температурному інтервалі між 4 K та 40 K. Число Лоренца кристалічного поля визначено з магнетних вкладів у тепло– та електропровідність. У результаті різкого впливу непружного розсіяння на теплові та електричні кінетичні коефіцієнти воно виявилось складною функцією температури.