Specific heat of europium

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The specific heat of a polycrystalline sample of europium (99.5%) is measured in the 80 to 850°K temperature range. A λ-anomaly in the specific heat (entropy change of 0.63 ± 0.05 cal/g-atom-degree) is observed at 765 ± 1°K and is due to a previously unknown phase transition. It is suggested that the transition is due to realignment of the electron structure of the metal. An antiferromagnetism-paramagnetism transition of the first kind occurs in the sample at 86.54 ± 0.02°K with a thermal hysteresis 0.06 ± 0.02°K and entropy changes 0.15 ± 0.01 cal/g-atom-degree.

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Europium (Eu) in the metallic state is characterized by an aggregate of physical and chemical properties that distinguish it greatly from "normal" rare-earth metals (REM) with incomplete 4f shells.[1] The crystal lattice of a "normal" REM can be regarded as a lattice of trivalent ions immersed in a stream of collectivized $5d^16s^2$ electrons. In Eu, the stabilization of the half-filled 4f shell causes the divalent state of the metal ($4f^75d^06s^2$) to be particularly stable. Therefore with respect to the type of lattice (bcc), the melting point (1099°K), the value of the metallic radius (2.04Å), the heat of sublimation (~42.2 kcal/g-atom), and a number of other properties, europium is more similar to divalent alkali-earth metals, particularly to barium (Ba). The similarity of the external electron shells of Eu($5d^06s^2$) and Ba($4d^{10}6s^2$) leads to a similarity of the energy band structures[2-3] and of the optical spectra[4] of the two metals. Using a divalent model of the metal, Rocher[5] attributed the stability of the "loose" bcc lattice of Eu to the contribution made to the binding energy by the exchange interaction via the conduction electrons. The notion that Eu is divalent at low temperatures agrees with the results of investigations of the magnetization of single crystals in strong magnetic fields,[6] the Mössbauer effect,[7] and electron paramagnetic resonance.[8]

Below $T_N = 90°K$, europium goes over into an antiferromagnetic state with helicoidal magnetic structure.[9] The average moment of the europium atom in this state is $5.9 \pm 0.4\ \mu_B$, somewhat lower than the $\mu_{theor} = 7\mu_B$ theoretically expected for $Eu^{2+}(^8S_{7/2})$, but definitely larger than for $Eu^{3+}(^7F_0)$.

The magnetic transformation in europium is a first-order phase transition. According to calorimetric[10] and Mössbauer[7] measurement data, the thermal hysteresis of the magnetic transition in europium does not exceed 0.3 deg. The abrupt change of the thermal-expansion coefficient and of the elastic moduli near T_N[11] is evidence of spontaneous deformation of the europium lattice when a helicoidal magnetic structure is produced. The change of the lattice parameters is, however, beyond the limits of the sensitivity of the x-ray diffraction method.[12] The magnitude of the volume effect of the transition, established by dilatometric means[7] is in poor agreement with the initial inclination of the phase-equilibrium line to the pressure axis[13,14] and with the entropy jump obtained calorimetrically by Gerstein et al.[10] The uncertainty of the thermodynamic and structural information makes it difficult to understand the nature of the magnetic first-order transition in Eu.

Information on the behavior of metallic europium at high temperatures is limited. The temperature dependence of the reciprocal magnetic susceptibility χ^{-1} of europium in the interval 300–1050°K[15] is shown in Fig. 1a. By investigating this dependence, Colvin et al.[15] came to the conclusion that the behavior of χ^{-1} above room temperature is not described by the simple model of isolated Eu^{2+} ions. One can separate on the χ^{-1} curve (Fig. 1a) a singular point at T ~ 760°K, which divides this curve into two parts. Above this point, the experimental curve is close to that calculated by van Vleck's theory for noninteracting $Eu^+(^9S_4)$ ions. The results of [15], which point to a complicated behavior of the magnetic susceptibility of europium above room temperature, allow us to assume that europium undergoes a certain phase transition at T ~ 760°K. The specific heat of metallic europium above room temperature has never been investigated before.

The purpose of the present study was to determine the temperature dependence of the specific heat of europium in the interval 80–850°K in order to verify the existence of a phase transition at high temperatures and to refine the thermodynamic characteristics of the first-order magnetic transition at low temperatures (the values of the temperature hysteresis and the transition entropy).

EXPERIMENTAL PROCEDURES AND RESULTS

The investigations were made on a sample weighing ~ 0.4 g, containing not less than 99.5% of europium (according to the data of the manufacturing plant), and having a resistance ratio R(293°K)/R(4.2°K) ≈ 40. The sample was cut and weighed in kerosene. During the course of these operations, the sample retained a bright surface. The procedure used to measure the specific heat of the high temperatures was similar to that used earlier for samarium.[16] The sample was wrapped in a tantalum foil and placed in an outgassed quartz ampoule, which was then filled with helium. The specific heats of the foil and of the sample were determined in a separate experiment and were taken into account in the calculation. The criterion for the reliability of the high-temperature measurements was the absence of irreversible changes in the residual resistivity, in the weight of the sample, and in the low-temperature specific heat after several heating and cooling cycles in the interval 300–850°K. The specific heat in the interval 80–300°K was determined by a previously described method.[17] The heat-exchange gas in these measurements was pure helium.

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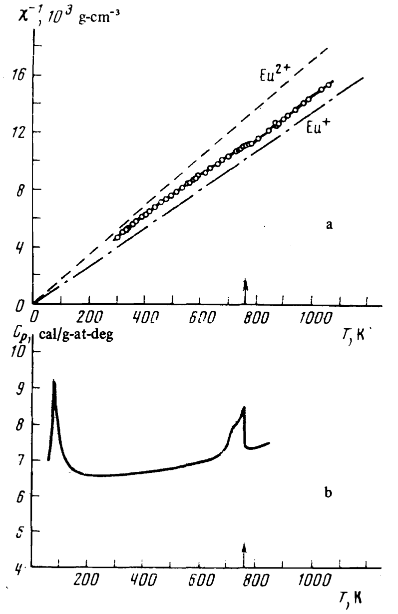

FIG. 1. Dependence of the reciprocal magnetic susceptibility [15](a) and of the specific heat (b) of europium on the temperature. The arrow indicates the transition temperature.

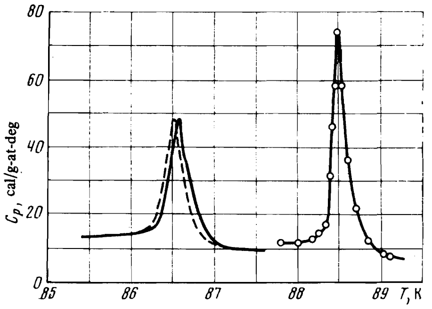

FIG. 2. Left–specific heat of investigated sample in the immediate vicinity of the Néel point after heating at a rate 0.15 deg/min (solid curve) and cooling at the same rate (dashed). Right–plot of δ-singularity of the specific heat in one of the samples investigated by Gerstein et al. [10]

The error in the values of $C_p(T)$ measured at high and low temperature is estimated at ±3%. The results of the measurements of the specific heat of europium heated and cooled at a rate ~0.15 deg/min are shown[1)] in Fig. 1b. The low-temperature branch of the Cp(T) curve agrees in the main with the results of earlier investigations.[10] A certain discrepancy is observed only in the region of the magnetic phase transition. The behavior of the specific heat of the investigated sample in the immediate vicinity of the first-order magnetic transition point is shown in the left-hand part of Fig. 2 (solid curve–heating, dashed–cooling); on the right in Fig. 2 is shown the plot of the δ-singularity of the specific heat near T_N, obtained by Gerstein et al. for polycrystalline europium ~99.6% pure. The critical point of the transition in our sample (86.54 ± 0.02°K) agrees with the transition point in a bulky sample of 99.9% purity, on which the volume effect of the magnetic transition in europium was measured by dilatometric means.[7] The results of the measurements have shown that at a temperature drift rate ~0.15 deg/min, the first-order transition is characterized by a hysteresis 0.06 ± 0.02 deg. The entropy change connected with the first-order transition (ΔS_{T_N} = 0.150 ± 0.010 cal/g-atom-deg) was calculated as the area under the plot of Cp against lnT in the interval between ~86 and 87°K. A similar reduction of the results of Gerstein et al.[10] was shown in Fig. 2, yields[2)] ΔS_{T_N} = 0.195 ± 0.016/g-atom-deg. The values ΔS_{T_N} = 0.195 – 0.150 cal/g-atom-deg at a transition volume effect $\Delta V/V = 2.1 \times 10^{-4}$ ($\bar{V}$ = 28.9 cm³/g-atom)[7] corresponds to initial inclination of the phase-equilibrium line to the pressure axis $dT_N/dP = \Delta V/\Delta S$ = (7 – 10) × 10^{-4} deg/cm²/kgf, in good agreement with the experimental $dT_N/dP = 9 \times 10^{-4}$ deg/cm²/kgf.[14]

The temperature dependence of the specific heat of Eu above room temperature (Fig. 1b) reveals a distinct λ anomaly with a discontinuity ΔCp ~ 1.2 cal/g-atom-deg at 765 ± 1°K without explicit symptoms of thermal hystersis. The base of the λ anomaly lies in the interval ~650 to 800°K. The character of the Cp singularity is such that it can be attributed to a continuous second-order phase transition. An estimate of the entropy increment due to the singularity of Cp at 765°K yields a value 0.63 ± 0.05 cal/g-atom-deg (the integral change of the enthalpy is ΔH = 47 ± 3 cal/g-atom).

DISCUSSION OF RESULTS

The calorimetric measurements confirm the assumption of the existence, at ~ 760°K, of a previously unknown phase transition in europium. There are in the literature additional indications of the possibility of a phase transition in europium above room temperature. In a study of the crystal structure of europium, Spedding et al.[18] observed an abrupt decrease of the coefficient of volume thermal expansion β in the temperature interval between 300 and 723°K (for example, at 300°K we have $\beta = 32.2 \times 10^{-6}$ deg^{-1}, and at 573°K we obtain $\beta = 19.2 \times 10^{-6}$ deg^{-1}). The anomalous behavior of the coefficient β was ascribed in [18] to the thermal excitation of the f electrons into the conduction band and to the associated increase of the density of the metal. It should be noted, however, that the electronic transitions f → (sd) or, equivalently, the conversion of some of the $E^{2+}(J = 7/2)$ ions into $Eu^{3+}(J = 0)$ ions has low probability, since it does not lead to a gain in the entropy connected with the uncertainty of the orientation of the total angular momentum, $\delta S = k \ln(2J + 1)$. On the other hand the (sd) → f transitions, which lead to an increase in the resultant angular momentum, should be accompanied by an increase rather than a decrease of the specific volume. The crystal structure of europium at temperatures above 723°K has not yet been investigated. Therefore the question of the thermal expansion of this metal between 723°K and the melting point (1099°K) remains open.

Owing to its high compressibility (~8.5 × 10^{-3} kbar^{-1} [19]) europium has already at ~ 40 kbar an atomic volume close to the volume of trivalent metal.[20] This could be attributed to partial filling of the vacant d shell of europium by f-state electrons located near the Fermi level. However, as shown by Coqblin and Blandin,[20] the f states in metallic europium are much farther from the Fermi level (~1 V) than in cerium or ytterbium (~0.1 eV), where the f → (sd) transitions actually take place under the influence of external pressure.

Stager and Drickamer[21] have established that in the temperature interval 37–296°K and at pressures 230–150 kbar europium undergoes a transition to a denser phase and this transition is accompanied by an electric-resistivity increase of approximately 40%. The phase transition occurring in europium at high pressures has not yet been explained. It is only obvious that this transition is not due to melting of the metal, inasmuch as the T−P melting curve of europium,[22] which has a maximum near $\sim$kbar is not extrapolated to room temperature at the pressures indicated above. The fact that europium and barium are isoelectronic gives grounds for assuming that the transformation in europium at high pressures is analogous to the transformation in barium at $P \sim 144$ kbar.[23] The T−P phase transition in europium,[21] when linearly extrapolated to normal pressure ($dT/dP \approx -3 \times 10^{-4}$ deg-cm^2/kgf), intercepts the temperature axis at the point $T \sim 760$°K ($P = 0$) which coincides with the point where the $\chi^{-1}(T)$ has a break and with the temperature anomaly of the specific heat.

Calculations of the band structure of europium in barium[2,3] have shown that a superposition of the d states with the (sp) bands of the valence electrons near the Fermi level is responsible for the bcc crystal structure of the metals and plays an important role in the determination of the shape of the Fermi surface. The Fermi surfaces of europium and barium turned out to be similar to the Fermi surface of tungsten—a typical d-transition metal. There are grounds for assuming that the phase transitions in europium and barium at high pressures, and also the transition in europium under normal pressure, are due to a shift of the s6 electrons of the conduction band to the energywise neighboring d-levels of these elements, with formation of denser and less compressible phases. The quantum-mechanical explanation of the possibility of such electronic transitions was first presented by Arkhipov.[24]

The solution of the question is the nature of the new phase transition in europium calls for additional data on the crystal structure of the metal at high temperatures and pressures, and also for reliable information on the band structure and on the position of the occupied $4f^7$ levels in the phonon spectrum of europium.

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1) The plots of the specific heat Cp(T) were calculated from thermograms registered with an automatic recording potentiometer.

2) Using a much larger integration interval (85 – 89°K), Gerstein et al. [10] obtained $\Delta S_{T_N} = 0.64$ cal/g-at-deg.

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