

GIANT THERMAL EXPANSION COEFFICIENTS IN RARE EARTH METALS AT LOW TEMPERATURES

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We have measured the thermal expansion of lanthanum, cerium, neodymium, gadolinium, and ytterbium from 1.5°K to 14°K, in order to look for anomalies corresponding to those found in the specific heat of Ce and Nd.^{1,2} The apparatus used is an optical-mechanical device that has been described elsewhere.³ Spectroscopic analysis of the raw material indicated a purity better than 99.5% for all the metals. Specimens were made by electron-bombardment melting into a tantalum form in high vacuum.

Usually large negative values of the linear thermal expansion coefficient, α , are observed for polycrystalline samples of Ce and Nd below the temperature of their first specific-heat maxima, i. e., at 12.5 and 7°K, respectively [Fig. 1(a)].

In contrast, the thermal expansion coefficient of La (polycrystalline, having predominantly the fcc phase) shows a normal temperature dependence above its critical temperature of 5.9°K. In the superconductive state α becomes negative [Fig. 1(b)]. Yb (fcc) has a normal behavior apart from a small anomaly around 2.3°K which may be due to an impurity (the specific heat of pure Yb shows no anomaly at this temperature⁴). It should be pointed out that the 4*f* shell in La is empty, whereas for Yb, it is filled. Ce, Nd, and Gd have 1,

3, and 7 4*f* electrons, respectively, in their atomic states. Gd shows an anomalous behavior in its polycrystalline form, in that the expansion coefficient changes sign twice below 12°K.

These anomalies in the thermal expansion may be discussed by considering the temperature dependence of the Grüneisen parameter

$$\gamma = 3\alpha/\kappa c,$$

where κ is the compressibility and c the specific heat per unit volume. The room-temperature values of γ for La, Ce, Nd, and Gd have been reported to be 0.29, 0.25, 0.42, and 0.63, respectively, in their polycrystalline form.⁵ For metals at low temperatures one can, in general, separate the electronic thermal expansion coefficient ($\propto T$) from the lattice thermal expansion coefficient ($\propto T^3$).^{3,4} By using known values of electronic and lattice specific heats, we can determine the electronic and lattice Grüneisen parameters γ_e and γ_L separately in this temperature range (room-temperature compressibilities have been used throughout for computation). For La we find in this way $\gamma_e = 0.6 \pm 0.8$ and $\gamma_L = 0.8 \pm 0.15$, the latter decreasing with temperature above 8°K. For Yb (ignoring the anomaly at 2.3°K) the results are $\gamma_e = -1.9 \pm 2.5$ and $\gamma_L = 1.04 \pm 0.1$. For Gd, no such separation

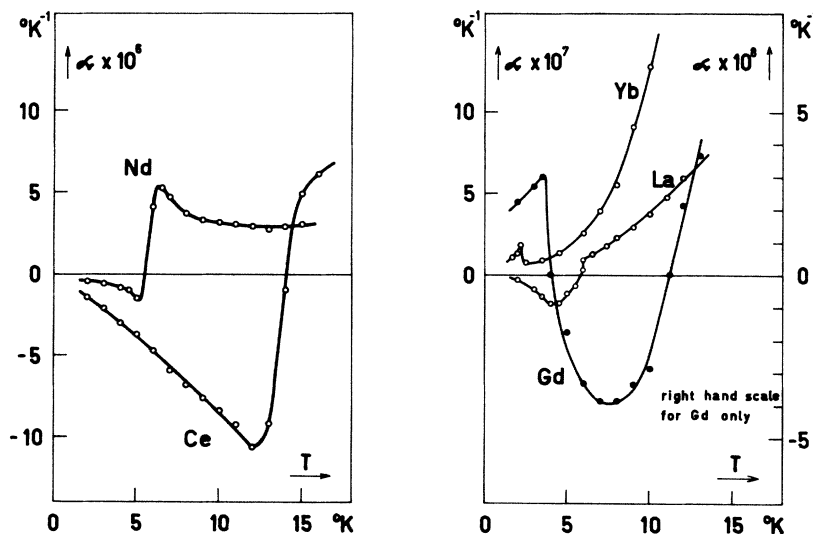


FIG. 1. Thermal expansion coefficient of polycrystalline rare earth metals at low temperatures.

of γ into two components can be made, but we find that the total γ has a value of 0.2 at 2°K, decreasing to a negative maximum of -0.1 at 10°K and then increasing again. We are not yet sure if this behavior is an intrinsic property of Gd or if there is an impurity effect superimposed, since specific heat measurements⁶ also show small anomalies which have been suggested to be possibly due to a Gd₂O₃ impurity.

The large thermal expansions of Ce and Nd occur together with specific-heat and susceptibility anomalies⁶ which are thought to be due to the 4*f* electrons present in these substances. Since the Debye temperatures and room temperature compressibilities of Ce and Nd are roughly equal to those of La, which shows no anomaly, we use $\alpha_{4f} = \alpha - \alpha_{La}$ and $c_{4f} = c - c_{La}$ to calculate approximately the Grüneisen parameter γ_{4f} of the 4*f* electrons alone. Here α and c are the observed expansion coefficient and specific heat of the metal considered, and α_{La} and c_{La} those of La. The temperature dependence of the so-determined γ_{4f} is shown in Fig. 2.

The similarity in shape of the two curves suggests similar properties of the 4*f* states in the two substances. Earlier discussions of the specific heat and susceptibilities^{1,2,7} of Ce and Nd postulated an antiferromagnetic ordering of the 4*f* spins in the hexagonal crystals to be the cause of the observed anomalies. The temperatures where this ordering sets in have been shown to be 12.5°K in Ce and 7°K in Nd (Nd shows an additional specific-heat peak around 19°K); they are near the zeros of γ_{4f} in Fig. 2.

It should be noted that Ce can have both a hexag-

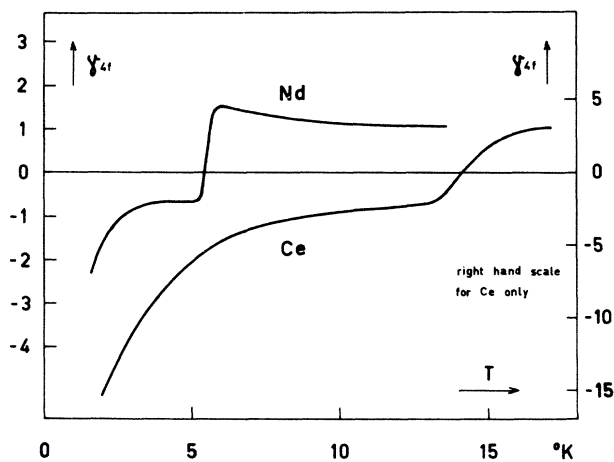


FIG. 2. Variation of the Grüneisen parameter of the 4*f* electrons (γ_{4f}) of Ce and Nd with temperature.

onal and a fcc structure at helium temperatures, the latter having a 15% smaller molar volume than the fcc room temperature modification.⁸ The specific-heat and susceptibility anomalies are known to occur only in the hexagonal phase. From dilatation measurements during cooling, it could be seen that the specimen investigated consisted of about 90% of the hexagonal phase. Since the expansion coefficient in the fcc phase is certainly smaller, the results in Figs. 1 and 2 can be taken to represent the properties of the hexagonal phase only. Recent neutron diffraction studies⁹ of hexagonal Ce at 4.2°K reveal an antiferromagnetic spin ordering consisting of ferromagnetic hexagonal layers with a +--+ stacking. Our results show that γ_{4f} is roughly constant above the temperature where the ordering sets in (12.5° for Ce and about 6° for our sample of Nd). For a model of independent particles, the Grüneisen parameter can be shown to be

$$\gamma = - \frac{V \sum_s (\partial E_s / \partial V) (\partial F / \partial T)}{\sum_s E_s (\partial F / \partial T)},$$

where E_s are the energy states of the particles (being only volume dependent), and f is their distribution function. For independent particles, γ cannot vary abruptly in a small temperature range. The temperature dependence of γ_{4f} is therefore in agreement with the view that above the ordering temperature, the 4*f* electrons tend to behave more or less like independent particles, whereas below this temperature, cooperative interactions become important leading to a strongly temperature-dependent Grüneisen parameter.

Its negative value can be interpreted qualitatively by saying that the quantity $(\partial/\partial V)(E_{dis} - E_{ord})$ is positive, where E_{ord} is the energy of the ordered antiferromagnetic ground state, and E_{dis} is the energy of a more disordered state at a nonzero temperature (below 12.5 or 6°, respectively). It is, of course, an open question whether it is mainly the c or the a axis of the hexagonal crystal which contracts on heating. It is interesting to note in this connection that a contraction of the c axis of the ferromagnetic hexagonal crystals of Gd, Tb, and Dy is observed,^{10,5} as these substances are heated through their Curie points, i. e., on destruction of the ferromagnetic ordering of their 4*f* spins.

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THERMAL CONDUCTIVITY AND ELECTRON SCATTERING AT INTERPHASE BOUNDARIES IN A SUPERCONDUCTOR

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It has long been realized that some scattering of electrons must occur at the normal-superconducting phase boundaries in the intermediate state. Such a scattering was suggested by Hulm¹ and in a modified form by Zavaritskii² to explain the maximum in the thermal resistivity in the intermediate state of superconductors discovered by Mendelssohn and Olsen³ and since observed by several other workers.⁴ A different mechanism has been shown to be responsible for the maximum where phonon conduction dominates in the superconducting state,⁵ but such an additional scattering of electrons in the intermediate state is required to explain the maximum where electrons dominate the thermal conductivity in both the normal and the superconductive states. No calculation based on the Bardeen-Cooper-Schrieffer (BCS) theory⁶ has, however, been reported so far for this case. We have now made such a calculation with the additional condition that the electronic mean free path in the normal state is longer than the scale, a , of the intermediate state structure. We have also made measurements on very pure indium specimens where these conditions hold, and find very good agreement with the predictions of our model.

Bardeen, Rickayzen, and Tewordt⁷ in their calculation of the thermal conductivity of a superconductor make use of an expression which applies generally, and which is valid under the assumption that the electrons are scattered elastically. They state that an energy interval dE gives the following contribution to the thermal conductivity κ for a given energy E relative to the Fermi energy E_F :

$$d\kappa = -[2N(0)v_0/3T]l(E)E^2(\partial f/\partial E)dE.$$

Here, $N(0)$ is the density of states at the Fermi level, v_0 is the velocity of electrons at the Fermi surface in the normal state, T is the temperature, $l(E)$ is the mean free path as a function of the energy, and $f(E)$ is the Fermi distribution function. This expression is quite independent of the density-of-states function and only requires a knowledge of $l(E)$. We may therefore apply it to the intermediate state as a whole. The problem then arises of the value of l to be used. It has been shown by Bardeen, Rickayzen, and Tewordt⁷ that under the condition of elastic scattering, $l(E)$ should be the same in the normal and in the superconducting states, and this has recently been proved directly by size-effect measurements by one of us.⁸ In the intermediate state, however, we have to take