Thermal Conductivities and Lorenz Functions of Dy, Er, and Lu Single Crystals*

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The thermal conductivity and electrical resistivity of Dy, Er, and Lu single crystals have been measured from 5 to 300°K. The Lorenz functions were calculated from the experimental results, and they exceeded the value expected for pure electron heat conduction. This indicated that phonons and/or magnons must contribute significantly to the heat conduction. At high temperatures the thermal conductivity was separated into suggested electron and phonon contributions. The magnetic transitions in Dy and Er produced an anisotropic effect on the thermal conductivity which is interpreted on the basis of magnetic superzones. A high-temperature anisotropy is explained by the anisotropic shape of the Fermi surface.

I. INTRODUCTION

THE transport properties of the heavy rare-earth elements exhibit many interesting features because of the various magnetic structures found in these elements. This paper presents an experimental study of the thermal conductivities and Lorenz functions of single-crystal Dy, Er, and Lu. In the temperature range covered, 4.2–300°K, these three elements display most of the various types of magnetic ordering found in the rare earths. For each of the three elements under study here measurements were made for heat flow along the [0001] direction (c axis) and along a direction in the basal plane. These elements all possess hexagonal symmetry.

Previously, thermal conductivity measurements[1–14] have been reported for polycrystalline heavy rare earths. These results have several common features; the thermal conductivities are small compared to non-rare-earth metals, the Lorenz functions obtained from experimental measurements of the electrical resistivity and thermal conductivity are considerably larger than expected for pure electron heat conduction, and anomalous behavior occurs at or near the various magnetic ordering temperatures. Edwards and Legvold[15] have measured the thermal conductivity of single-crystal Tm. Their results are similar to those described here.

The purposes of the present measurements were to look for anisotropy effects due to the magnetic ordering and due to the anisotropic nature of the Fermi surface of the heavy rare earths,[16,17] to identify the heat carriers involved, and to study the important scattering mechanisms limiting the heat conduction.

II. EXPERIMENTAL PROCEDURE

The single crystals were grown from arc-melted buttons using the strain anneal method described by Nigh.[18] The orientations of the crystals were determined by back-reflection Laue techniques. Then samples were cut in the form of rectangular parallelepipeds by the spark-erosion method. The sample cross sections were about 2×2 mm and the length varied from 5 to 17 mm. Two samples were prepared for each element. One was oriented with the [0001] direction (or c axis) along the sample axis, the other with either the $[11\bar{2}0]$ direction (a axis) or $[10\bar{1}0]$ direction (b axis) along the sample axis. The Dy c axis and the Er samples were grown by Sill and used in the thermoelectric power measurements of Sill and Legvold.[19] An analysis of selected impurities and resistivity ratios is included in Table I.

The thermal conductivity measurements were made by the steady-state heat flow method. The apparatus used was similar to that described by Colvin and Arajs.[4] The sample holder consisted of an outer copper can which was placed in contact with a cryogenic liquid and an inner copper heat sink. Two small pure copper rods were soldered with pure indium to the ends of the sample. Thermocouple junctions were soldered into holes in the rods located adjacent to the sample.

* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission, Contribution No. 2286.

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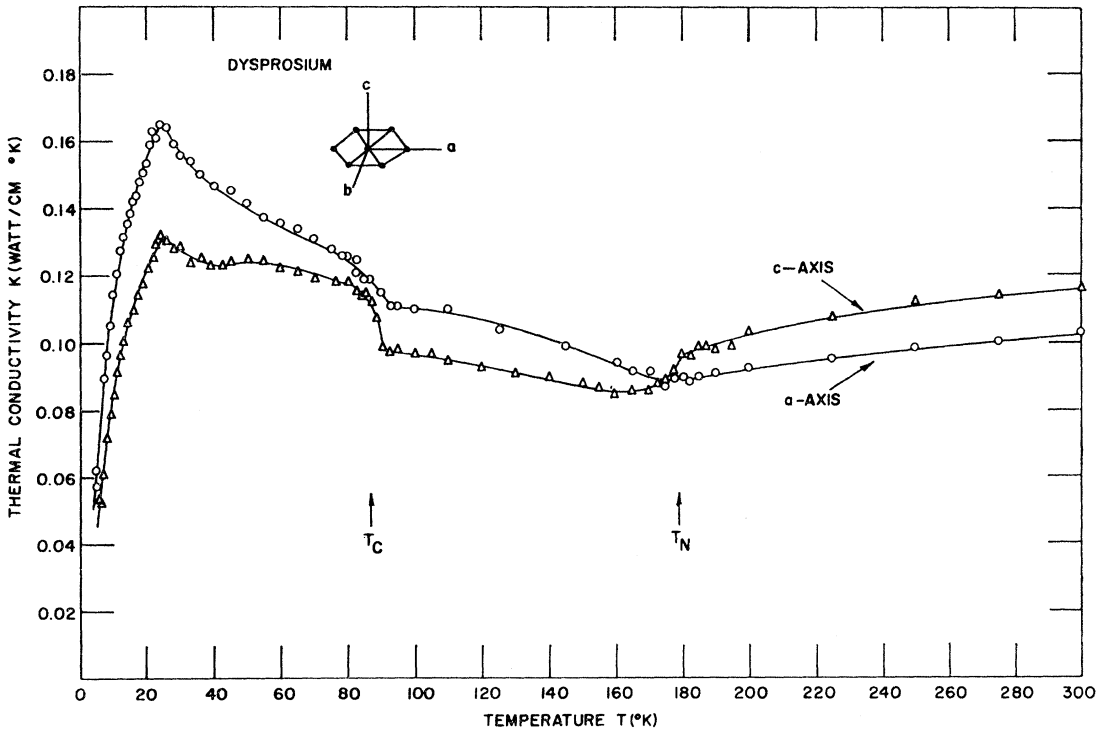

FIG. 1. The thermal conductivity as a function of temperature for dysprosium.

One of the rods was then clamped to the heat sink. A small electrical heater was clamped to the other rod.

The temperature range from 4.2 to 300°K was covered in three steps. The data were taken in the following order: 4.2–25°K using liquid helium as the bath, 20–85°K using liquid hydrogen, and 80–300°K using liquid nitrogen. The temperature of the heat sink was controlled by an electrical heater and sensing device.

The absolute sample temperatures and the temperature differences were determined by thermocouples. Au–0.03% Fe versus Cu thermocouples were used in the temperature range 4.2–30°K. Constantan versus Cu thermocouples were used in the range 20–300°K. The thermocouple leads were carefully thermally grounded onto the heat sink to minimize heat conduction along the thermocouple wires. An ice bath was used as the reference temperature. The temperature difference across the sample was determined by feeding the output voltage of the thermocouples attached at either end of the sample into a Dauphinee potential comparator.[20] The output of the comparator was measured using a Rubicon model 2771 thermofree microvolt potentiometer. Temperature differences were typically 1–2°K.

In order to minimize heat losses by convection the sample chamber was evacuated to a pressure of about 5×10^{-6} Torr. To minimize radiation losses, the sample was surrounded by a radiation shield held at the temperature of the sink. Correction for radiation and electrical lead conduction losses were made using a method described by Norén and Beckman.[21] The results are expected to be within 6%. The primary difficulty arises because of the low conductivity of the rare earths; this makes small heat losses important.

Electrical resistivity measurements were made by the standard four-probe measurements described by Colvin *et al.*[22] The absolute error was estimated to be less than 3%.

III. RESULTS

The observed temperature variation of the thermal conductivities of Dy, Er, and Lu are shown in Figs. 1–3. The magnetic ordering temperatures of Dy and Er as determined by neutron diffraction studies[23,24] are

TABLE I. Selected sample impurities and resistivity ratios.

Sample (axis)	Impurities (ppm by weight) Fe	O_2	Ta	$R_{300°K}/R_{4.2°K}$
Dy *a*	100	157	400	24.2
c				13.4
Er *b*	150	235	500	17.4
c	900	280	<500	10.1
Lu *b*	$\lesssim30$	128	$\lesssim200$	28.9
c	$\lesssim30$	99	$\lesssim200$	45.7

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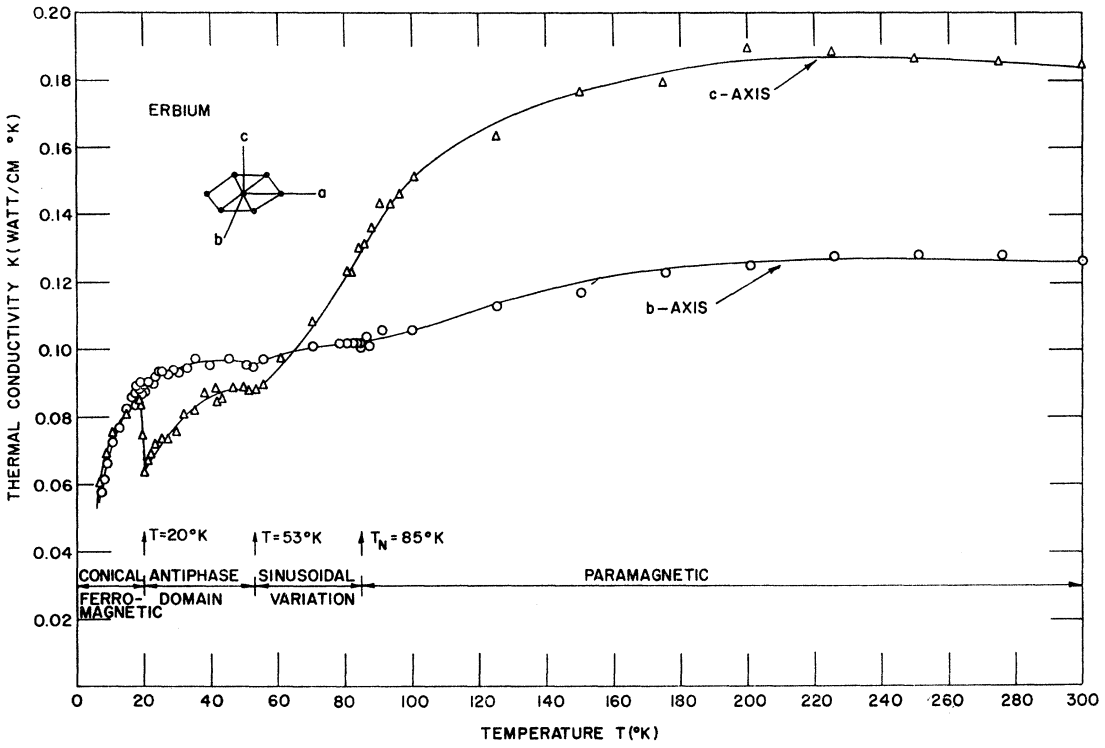

FIG. 2. The thermal conductivity as a function of temperature for erbium.

also indicated. Figure 4 shows a pictorial summary of the magnetic moment behavior of Dy and Er as determined by the neutron diffraction work.

Anisotropy was evident in all the elements studied. In the paramagnetic temperature range the c-axis thermal conductivity, K_c, divided by the basal plane conductivity (K_a or K_b) was 1.1, 1.5, and 1.7 for Dy, Er, and Lu, respectively. The polycrystalline results at 300°K of Powell and his co-workers[6,7,12] lie between the results for the basal plane and the c axis reported here. A second type of anisotropy due to the magnetic ordering occurred in Dy and Er. The c-axis thermal conductivity of both elements dropped sharply as the temperature of the sample was increased through the ferromagnetic-antiferromagnetic transition temperature T_c. As the Néel temperature T_N was approached, the c-axis thermal conductivities began to rise rapidly and underwent a change of slope near T_N. Only slight effects were seen in the basal-plane results for Dy and Er.

The temperature dependence of the thermal conductivity of nonmagnetic Lu was similar to results for non-rare-earth metals. However, Lu, Dy, and Er all have thermal conductivities much smaller than most metals.

The temperature variation of the electrical resistivities of Dy and Lu is shown in Figs. 5 and 6. The results for Er (not shown) agreed well with those of Green *et al.*[25] The Dy results are in good agreement with the unpublished work of Jew.[26] The electrical resistivities of our particular Dy and Er crystals were measured in order to obtain accurate calculations of the Lorenz function. The temperature dependence of the electrical resistivity of Lu was similar to most non-rare-earth metals. Below 5°K the resistivity was constant. In the temperature range 5–20°K the resistivity could be expressed by

$$\rho=\rho_0+\alpha T^n, \tag{1}$$

where ρ_0 was the residual resistivity and n was 3.2 for the c-axis results and 2.9 for the b-axis results. Above 200°K the resistivities for both axes varied linearly with the temperature.

The Lorenz function given by

$$L=K\rho/T, \tag{2}$$

where K and ρ are the measured thermal conductivity and electrical resistivity, respectively, is shown as a function of temperature in Figs. 7–9. The values obtained for all except the c-axis Lu crystal are anomalously large.

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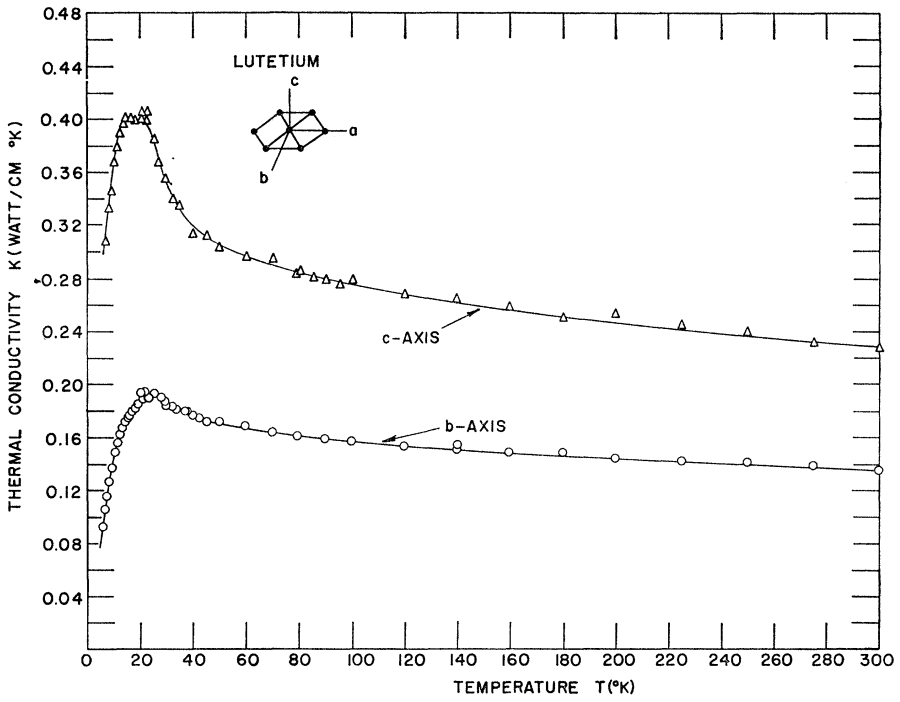

FIG. 3. The thermal conductivity as a function of temperature for lutetium.

IV. DISCUSSION

The theory of thermal conduction in pure metals has been reviewed by Klemens[27] and by Mendelssohn and Rosenberg.[28] The basic theoretical problem is to understand the scattering mechanisms which impede the motion of electrons through the solid. In pure metals, phonons may also contribute significantly to the heat flow. The magnetically ordered rare-earth metals have still another possible heat carrier—the magnons. A complete theoretical treatment applicable to the rare earths has not been developed, so the discussion must be qualitative and the separation of the conductivity into phonon, magnon, and electron parts is only suggestive.

The theory of *pure electron heat conduction*[27] predicts that the Wiedemann-Franz law should be obeyed for very low temperatures and possibly for temperatures above Θ_D, Θ_D being the Debye temperature. In these temperature regions the scattering is elastic, and the Lorenz function should equal the Lorenz number ($L_0 = 2.4453\times10^{-8}$ W Ω °K^{-2}). This is experimentally well established for many pure metals.[27] Θ_D is about 160°K for the metals investigated here.[29] Our results show that L exceeds L_0 throughout the temperature range 4.2–300°K with the exception of the Lu c-axis sample. It is therefore necessary to assume that phonons and/or magnons contribute significantly to the heat conduction. The total thermal conductivity can be expressed as

$$K = K_e + K_g + K_m, \quad (3)$$

where e, g, and m refer to electrons, phonons, and magnons, respectively. Specific-heat measurements on

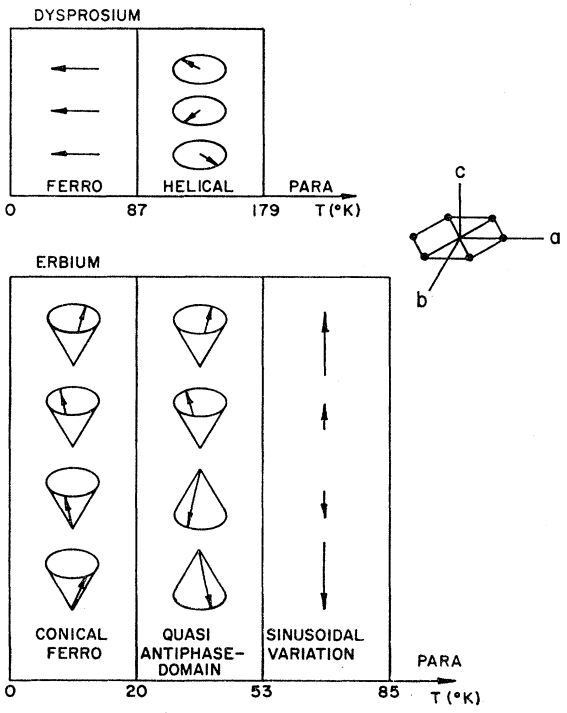

FIG. 4. Ordered spin structure observed by neutron diffraction.

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[28] K. Mendelssohn and H. M. Rosenberg, in *Solid State Physics*, edited by F. Seitz and T. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 223.
[29] K. A. Gschneidner, *Rare Earth Alloys* (D. Van Nostrand, Inc., Princeton, N. J., 1961), p. 38.

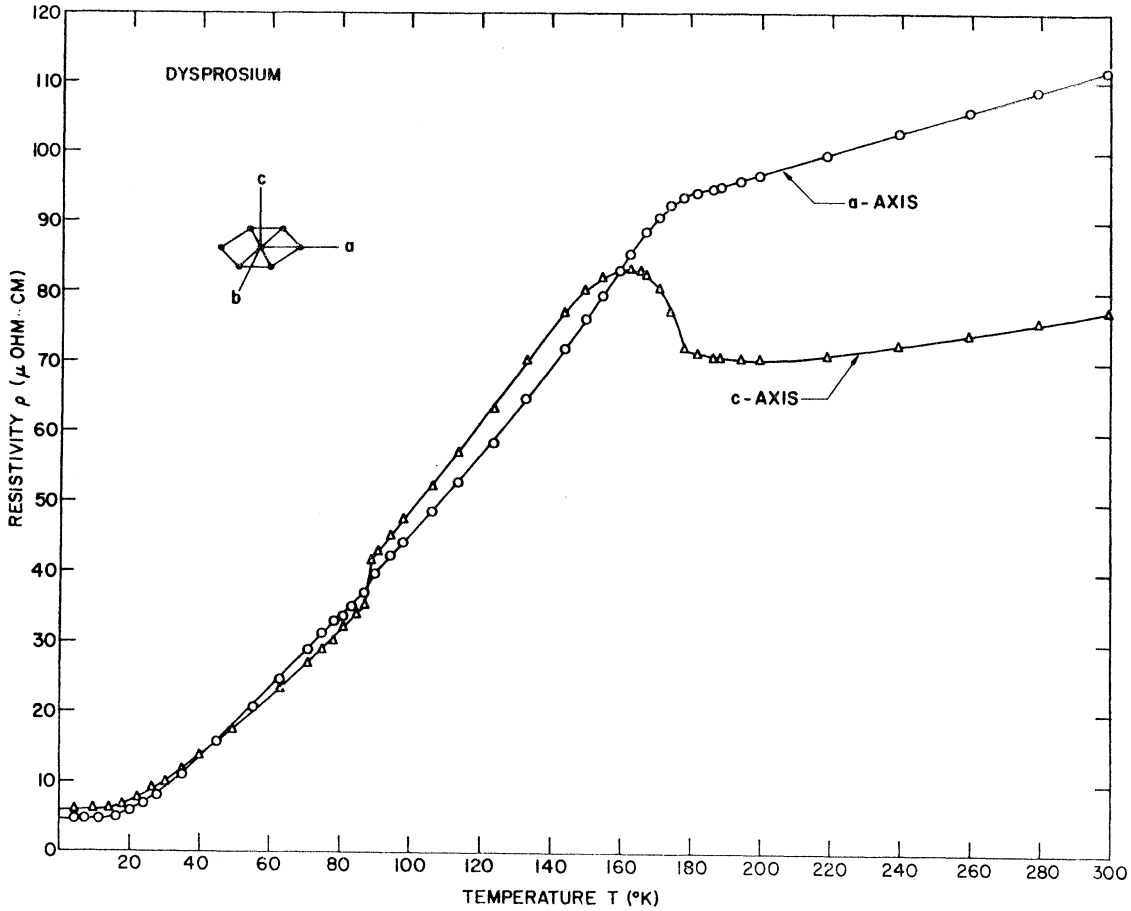

FIG. 5. The electrical resistivity as a function of temperature for dysprosium.

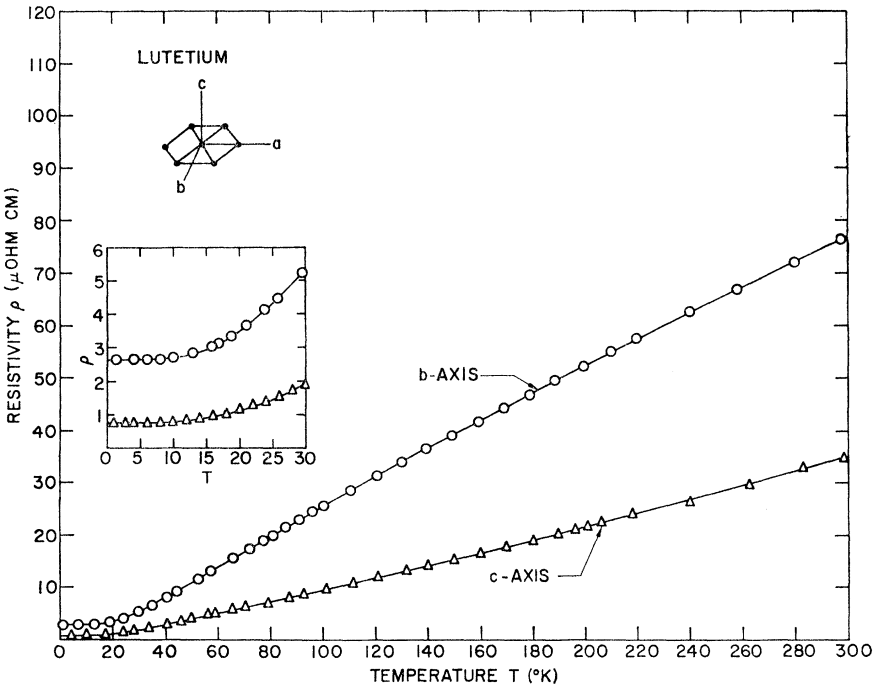

FIG. 6. The electrical resistivity as a function of temperature for lutetium.

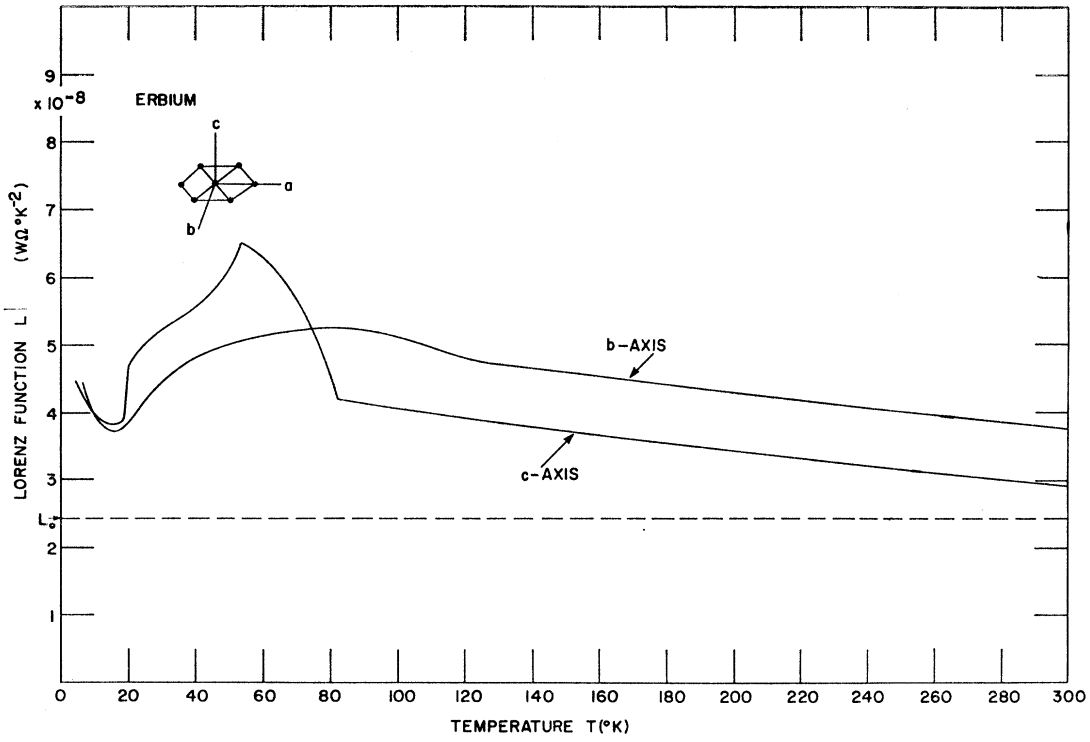

FIG. 7. The calculated Lorenz function for erbium.

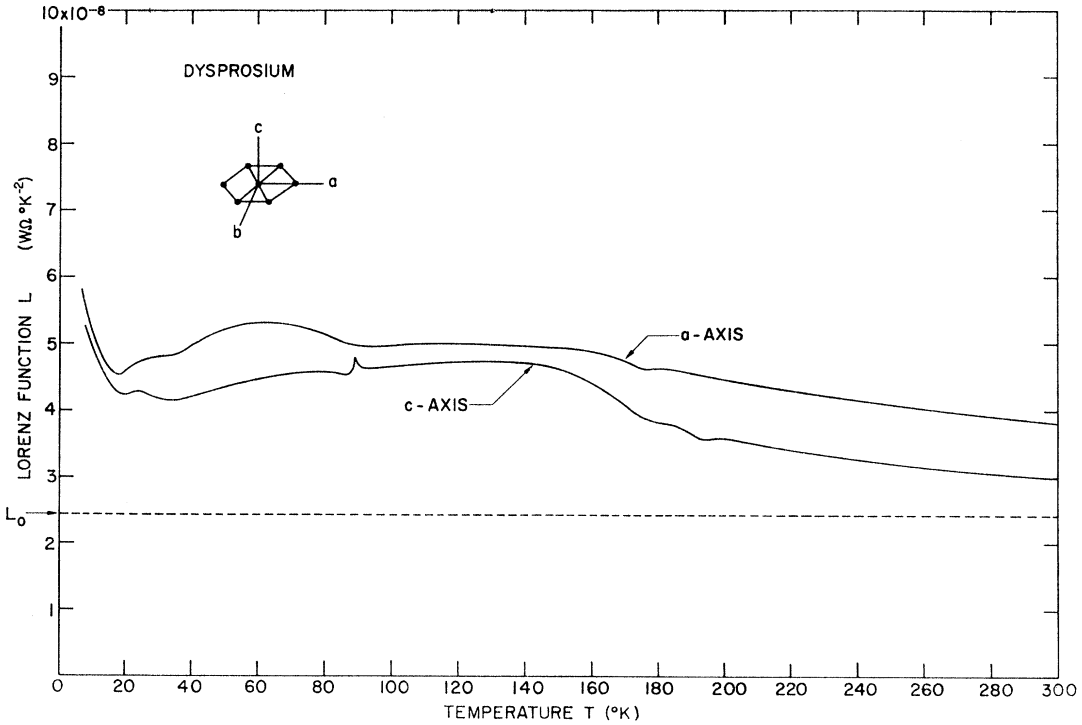

FIG. 8. The calculated Lorenz function for dysprosium.

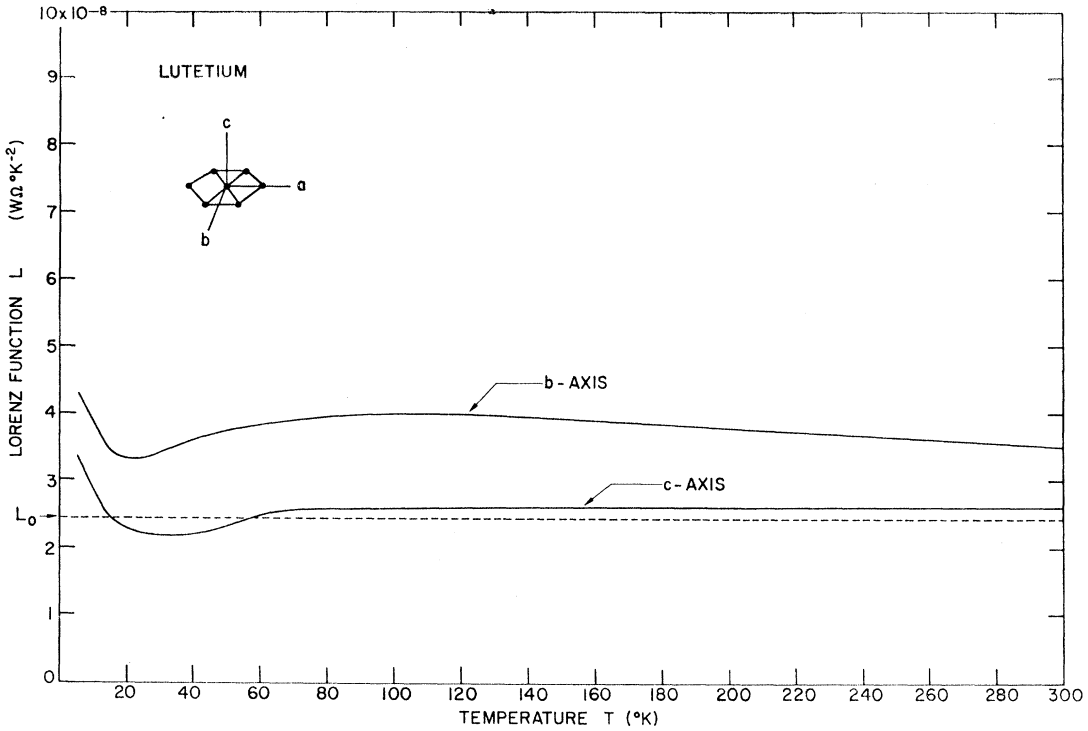

FIG. 9. The calculated Lorenz function for lutetium.

the heavy rare earths by Lounasmaa and Sundstrom[30] show that magnons can contribute significantly to the total specific heat above 5°K. It would correspondingly not be improbable that magnons could carry a significant amount of the heat.

Separation of the measured thermal conductivity into its components was possible only for temperatures above Θ_D. Above about 200°K, K_e was determined from the Wiedemann-Franz law

$$K_e(\text{ideal}) = L_0 T/\rho, \tag{4}$$

where ρ was the experimentally determined electrical resistivity. Figure 10 shows a plot of K–K_e versus T^{-1} for temperatures above 200°K. In this region K_m may be neglected, and the linear results of Fig. 10 weakly suggest that the remaining contribution to K is due to phonon conduction limited by phonon-phonon scattering. Table II lists the magnitudes of K, K_e, and $K-K_e$(ideal) at 300°K. The results for $K-K_e$(ideal) are consistent with those of Jolliffe *et al.*[12]

TABLE II. Components of K at 300°K.

Sample	K (W/cm °K)	K_e (W/cm °K)	$K-K_e$ (ideal) (W/cm °K)
Dy a	0.103	0.066	0.037
c	0.116	0.095	0.021
Er b	0.127	0.082	0.045
c	0.184	0.153	0.031
Lu b	0.136	0.095	0.041
c	0.228	0.211	0.017

It is admittedly risky to attempt this separation,[27] since we are not sure if we are sufficiently above Θ_D to assume the validity of the Wiedemann-Franz law. The quantity $K-K_e$(ideal) should give a lower bound to K_g, and would be expected to be a better result at the higher temperatures.

We attempted to separate the thermal conductivity into its component parts in the temperature range 4.2–20°K by again assuming that K_e would be given by the Wiedemann-Franz law. K_e was then subtracted from the measured thermal conductivity. The remaining contribution showed a complex temperature dependence, and it was impossible to separate the heat carriers and determine the scattering mechanisms involved.

The anomalous behavior of the electrical resistivity of the magnetically ordered rare earths at T_c has been interpreted by Mackintosh,[31] Elliott and Wedgwood,[32]

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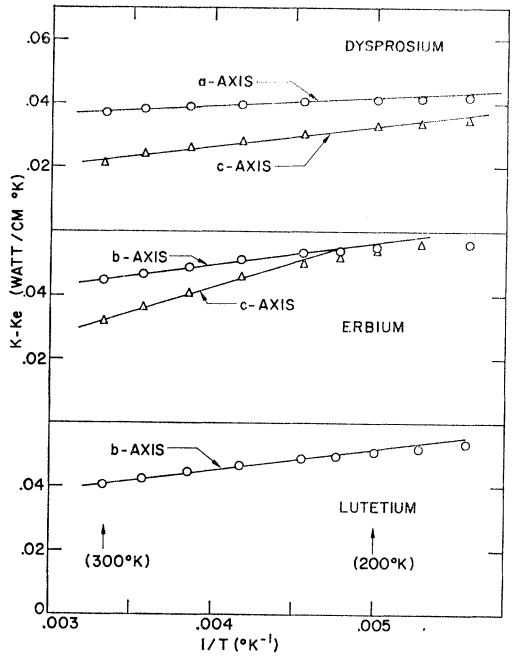

FIG. 10. $K-K_e$ versus T^{-1} for dysprosium, erbium, and lutetium.

and Miwa[33] on the basis of magnetic superzones. They point out that at the onset of antiferromagnetic ordering (at T_c) a magnetic periodicity differing from the ionic lattice periodicity is introduced in the c-axis direction. This magnetic periodicity introduces planes of energy discontinuity called magnetic superzones. These superzones destroy parts of the Fermi surface normal to the c axis, but leave components of the Fermi surface in the basal plane relatively unchanged. Both the electrical and the thermal conductivities (K_e) depend on integrals over the Fermi surface like

$$K_{ij},\ \sigma_{ij} \sim \int_{\text{F.S.}} v_i dS_j, \tag{5}$$

where v_i is the ith component of the electron velocity and dS_j is an element of surface in the j direction. As the sample temperature is increased through T_c, parts of the Fermi surface in the c-axis direction are destroyed, and an abrupt drop in the electrical and thermal conductivities of erbium and dysprosium is observed. Near, but below, T_N the c-axis thermal conductivity rises, presumably due to a reduction in the magnetic energy gaps. The basal-plane results are relatively unaffected because the energy gaps do not have a large effect on the Fermi surface in the basal-plane direction. Loucks and Liu[34] have calculated the effective change in the Fermi surface area of Er when superzones are introduced and find that

$$\Delta A_c = 6\%,$$
$$\Delta A_b \sim 0.6\%. \tag{6}$$

From Fig. 1 the experimental results for Dy are $\Delta K_c \sim 10\%$ at T_c and T_N and $\Delta K_a \sim 1\%$ at both T_c and T_N. For erbium the rapid changes in K preclude measurements.

In the paramagnetic temperature region the c-axis thermal conductivity always exceeds the basal-plane conductivity. Edwards and Legvold[15] suggest this is due to the anisotropic shape of the Fermi surface. The projected area of the Fermi surface in the c direction is greater than the projected area in the basal-plane directions, i.e.,

$$\int_{\text{F.S.}} dS_c > \int_{\text{F.S.}} dS_{a,b}. \tag{7}$$

Hence, from Eq. (5) it follows that (for the electron heat carriers)

$$K_c > K_{a,b}, \tag{8}$$

assuming that v_c and $v_{a,b}$ may be replaced by some average velocity. Loucks and Liu[34] have calculated the ratio of the projected areas of the Fermi surface for Er and find that

$$A_c/A_b = 2.1. \tag{9}$$

This compares reasonably well with the experimental K_c/K_a of 1.5 for Er and very well with the 1.8 found for Lu. The result of 1.1 for Dy suggests that here the scattering must be somewhat different.

ACKNOWLEDGMENTS

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[33] H. Miwa, Progr. Theoret. Phys. (Kyoto) **29**, 477 (1963).

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