SOVIET PHYSICS JETP VOLUME 28, NUMBER 4 APRIL, 1969

THERMAL CONDUCTIVITY OF POLYCRYSTALLINE AND MONOCRYSTALLINE TERBIUM BETWEEN 1° AND 4°K

A. G. KARAGEZYAN and K. V. RAO

Erevan State University and Oxford University

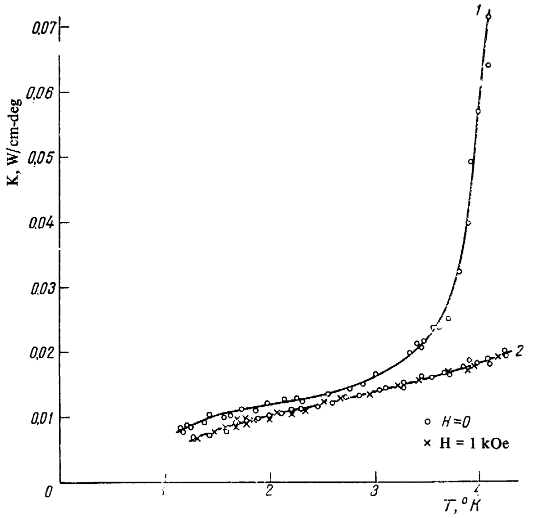
Submitted April 13, 1968

Zh. Eksp. Teor. Fiz. 55, 1168–1172 (October, 1968)

Anomalies in the thermal conductivity of polycrystalline and single-crystal samples of terbium are observed in liquid helium temperatures. The thermal conductivity of a terbium single crystal in a magnetic field is measured to study magnetic anisotropy effects. The electric and thermal conductivity measurements of the single crystal yield 2.55×10^{-8} W-ohm/deg^2 for the Lorenz number; this is the smallest value ever observed for rare-earth metals at 4.2°K. An attempt is made to explain the observed anomalies by effects associated with the presence of impurities in these metals.

IT is well known that thermal conductivity in ordinary metals at temperatures far below the Debye temperature Θ is governed predominantly by the scattering of conduction electrons on impurities and is proportional to the absolute temperature. However, our data for all rare-earth ferromagnets[1-4] are not consistent with this simple picture.

Other investigations[5,6] also show that in the region of residual electrical resistance ($\rho = \rho_0$) the calculated Lorenz numbers (defined as $K\rho_0/T$, where K is the thermal conductivity) are about three times as large as the theoretical value 2.45×10^{-8} W-ohm/deg^2. It has therefore been suggested[1-6] that the total thermal conductivity must include, in addition to its electronic part, a magnon mechanism and other possible mechanisms of heat transport; the analysis of experimental data is thereby complicated considerably. A further difficulty arises because in rare-earth ferromagnets considerable magnetocrystalline anisotropy exists. Thus at low temperatures terbium in its ferromagnetic state exhibits high uniaxial anisotropy, with the direction of easy magnetization lying in the basal plane.[7,8] Through the combined effects of crystal field anisotropy and spin–orbit coupling, at liquid helium temperatures the spins are pointed in the basal plane by effective fields of the order of 600 kilogauss. In the basal plane "preference" between the easy axis b [$10\bar{1}0$] and the hard axis a[$11\bar{2}0$] is expressed by a field of about 10^3 gauss.[9]



Temperature dependence of thermal conductivity in terbium. 1—polycrystal, 2—single crystal (with c axis and crystal axis forming 78° angle).

The aforementioned anisotropy seriously affects the magnetic structure and can produce an energy gap in the spin wave spectrum.[10-13] This gap appears to play a definite role in the behavior exhibited by the thermal conductivity of rare-earth ferromagnets at low temperatures. It is therefore clear that by investigating the thermal conductivity of magnetic solids, and particularly the rare-earth ferromagnets, in magnetic fields at low temperatures we can, in principle, obtain definite information about that portion of the thermal conductivity which results from electron scattering on magnons. However, it is difficult to interpret such investigations of polycrystals, where the role of magnetocrystalline anisotropy remains entirely uncertain in the given case. Obviously, therefore, studies of single crystals, which permit comparative easy analysis of the results, are extremely useful.

We measured the temperature dependence of thermal conductivity in polycrystalline and monocrystalline terbium samples at temperatures 1–4°. For the single crystal the thermal conductivity was also measured in an external magnetic field. In addition, the electrical resistance of both the polycrystal and the single crystal was measured at 4.2°K and at room temperature.

The polycrystal was a wire 3.2 cm long with 1.47-mm mean diameter. The single crystal was grown in the form of a cylindrical rod 6.2 cm long with 3.78-mm mean diameter,[1] using the zone melting technique in an argon atmosphere. The hexagonal angle c in the single crystal formed an angle of about 80° with the sample axis. The temperature gradient was determined with a differential Chromel-gold thermocouple (+0.03 at.% iron). The apparatus, which has been described in [3], permitted measurements with at most 1% error.

---

[1] The polycrystal was grown by Johnson, Matthey and Co., Ltd., and the single crystal by Metals Research, Ltd.

The accompanying figure shows the thermal conductivities of the crystals as functions of temperature. The polycrystal exhibits a rapid decrease just below 4.2°K, and a gradual but fully determinable change in the slope of the curve from 3.5° to 2°K.

The thermal conductivity of the single crystal was measured at $H = 0$ and 1000 Oe. In the region 221–229°K terbium is known to be in an antiferromagnetic state that can be destroyed in a critical field of about 200 Oe, which transforms terbium from its antiferromagnetic to its ferromagnetic state.[14] Therefore, before cooling the sample from room temperature to the desired temperature we applied a 1-kOe external field parallel or antiparallel to the single-crystal axis, as required, to align the spins along a given direction. Since the c axis formed an angle of about 80° with the crystal axis and the conduction electrons participating in thermal conductivity therefore moved (because of the temperature gradient) almost in the basal plane, this experiment represented a very interesting study of effects resulting from anisotropy in the basal plane.

The figure reveals no appreciable effect of the magnetic field on the thermal conductivity of the terbium single crystal. The temperature dependences of the polycrystalline and single-crystal thermal conductivity exhibit overall mutual similarity below 2.8°K, but differ greatly at higher temperatures.

When we compare our results for the polycrystal with data given in [5], where the thermal conductivity of two polycrystalline terbium samples was measured in the region 2–100°K we find the following contrast: In [5] a pronounced minimum of the thermal conductivity is observed in the region 2–4°K, whereas our curve undergoes a change of slope at about 1.5°K and appears to pass through the coordinate origin.

It seems impossible, at the present time, to account uniquely for the foregoing contrast or the anomalies on the thermal conductivity curves. However, the data on the thermal conductivity of terbium that are given in [15, 17] suggest certain hypotheses. In [15–17] we find indications that anomalies exist in the region 1.4–4°K; the different investigators attribute these anomalies to excess entropy that is generated when the terbium ground state is split in the crystal field which is present within a sample of the oxide Tb_2O_3. On the other hand, magnetic susceptibility measurements[18] present the characteristic features of antiferromagnetic ordering in Tb_2O_3 at 2.42°K. All these results have suggested that the aforementioned anomalies are associated with the presence of Tb_2O_3 impurity. One is therefore tempted from purely dimensional considerations to associate the thermal conductivity anomalies with localized electron states existing near impurity centers and having centers and having energies close to the Fermi energy of the solvent. When we also consider that the oxygen impurity may be distributed differently in the various samples, we can apparently account for the aforementioned discrepancies.

On the other hand, the calculations in [17] showed the following components of the total thermal conductivity in terbium at 5°K: 7% magnetic, 51% electronic, 33% lattice, and 9% nuclear. Also, when the magnetic part of the internal energy falls off exponentially below 4°K, the nuclear magnetic energy comes into play. The nuclear component of the thermal conductivity is inversely proportional to the absolute temperature and strongly enhances the total thermal conductivity below 2°K. The role of this new term in transport phenomena is still not understood.

The anomalous behavior of thermal conductivity in polycrystalline terbium at about 3.8°K seems to be caused by an energy gap in the spin-wave spectrum; calculations in [13] show that this gap appears in terbium at about 20°K. The several mentioned factors are probably among the possible causes of the anomalies, even if they are not the only ones. At the same time, measurements on the single crystal suggest that magnetic crystal anisotropy also plays an important part in the thermal conductivity of terbium. Thus, if we assume the "effective" direction of the single-crystal axis to have lain in the basal plane, then the large difference between the thermal conductivities of the polycrystal and single crystal around 4°K can be associated in some manner with the anisotropy that exists between the c axis and the basal plane.

As already mentioned, the external magnetic field did not appreciably influence the behavior of the single-crystal thermal conductivity. This negative result may signify that the applied field was too weak to produce an effect because either the basal anisotropy energy (equivalent to a 1-kG field), or demagnetizing fields, or both, were actually greater than was anticipated, so that the spins were not aligned to the necessary extent or even not at all.

The anisotropy can evidently not be associated with the scattering mechanism that is characteristic of electrical resistance. We know that at helium temperatures the temperature-dependence curves of the Lorenz number exhibit anomalies that are not found in any electrical resistance data published up to the present time. The table gives high values of the Lorenz number, $(5-7) \times 10^{-8}$ W-ohm/deg^2, for polycrystals, whereas the value 2.55×10^{-8} W-ohm/deg^2 for the single crystal is quite close to the theoretical value obtained for ordinary metals.

However, it has been shown[3, 4] that for rare-earth ferromagnets we cannot use the equations which are suitable for analyzing the conductivity of ordinary metals. A comparison of the residual electrical resistance, the thermal conductivity, and the resistivity ratio $\rho(293^\circ K)/\rho(4.2^\circ K)$ for the polycrystals and the single crystal shows that our single crystal contained more impurities than the polycrystals which are mentioned in the table. For rare earth metals a large Lorenz number usually corresponds to high residual resistivity, but this rule evidently does not apply to the single crystal.

Source	Sample	Resistivity Ratio $(293^\circ K)/\rho(4{,}2^\circ K)$	Residual resistivity ($\mu\Omega$-cm)	Lorenz number at 4.2°K (10^{-8} W-ohm/deg^2)
Aliev and Volkenshtein [5]	Polycrystal (1)	30,0	4,13	5,16
	Polycrystal (2)	15.6	7,9	5.33
Arajs and Colvin [6]	Поликристалл	25.77	4,85	7,0
Our data	Polycrystal	26.54	4,903	7,3
	Single crystal	20,1	5,35	2,55

The possibility exists that at helium temperatures the transport behavior of rare-earth metals resembles that of ordinary metals, at least in the basal plane.

In conclusion, the authors wish to thank Professor K. Mendelsson for his constant interest, Professor F. Keffer for a valuable discussion of the results, and Professor D. M. S. Bagguley for furnishing the terbium single crystal. One of the authors (A. G. Karagezyan) thanks the British Council and the Ministry of Higher and Intermediate Special Eduction of the U.S.S.R. for enabling him to work at Oxford University.

---

[1] K. V. Rao, Phys. Lett. **24A**, 39 (1967).

[2] A. G Karagyozyan and K. V. Rao, Phys. Lett. **25A**, 235 (1967).

[3] A. G. Karagyozyan, K. Mendelsson, and K. V. Rao, Proc. Roy. Soc. (London) (to be published).

[4] K. V. Rao, Thesis, Oxford University, 1967.

[5] N. G. Aliev and N. V. Volkenshtein, Zh. Eksp. Teor. Fiz. **49**, 24 (1965) [Sov. Phys.-JETP **22**, 17 (1966)].

[6] S. Arajs and R. V. Colvin, Phys. Rev. **136**, A439 (1964).

[7] W. C. Koehler, H. R. Child, E. O. Wollan, and J. W. Cable, J. Appl. Phys. **34**, 1335 (1963).

[8] J. J. Rhyne and A. E. Clark, J. Appl. Phys. **38**, 1379 (1967).

[9] J. L. Stanford and R. C. Young, Phys. Rev. **157**, 245 (1967).

[10] A. Yoshimori, J. Phys. Soc. Japan **14**, 807 (1959).

[11] T. A. Kaplan, Phys. Rev. **124**, 329 (1961).

[12] K. Niira, Phys. Rev. **117**, 129 (1960).

[13] A. R. Mackintosh, Phys. Lett. **4**, 140 (1963).

[14] K. P. Belov, R. Z. Levitin, and S. A. Nikitin, Usp. Fiz. Nauk **82**, 449 (1964) [Sov. Phys.-Usp. **7**, 179 (1964)].

[15] O. V. Lounasmaa and P. R. Roach, Phys. Rev. **128**, 622 (1962).

[16] R. M. Stanton, L. D. Jennings, and F. H. Spedding, J. Chem. Phys. **32**, 630 (1960).

[17] O. V. Lounasmaa and L. J. Sundström, Phys. Rev. **150**, 399 (1966).

[18] V. S. Gerstein, F. J. Jelinek, and F. H. Spedding, Phys. Rev. Lett. **8**, 425 (1962).

Translated by I. Emin
130