Zeitschrift: Helvetica Physica Acta

Band: 41 (1968)

Heft: 6-7

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DOI: https://doi.org/10.5169/seals-113971

Thermal Conductivity of Europium Oxide (EuO) Across the Curie Temperature[1])

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(10. IV. 68)

Abstract. Results of measurements of the thermal conductivity K of a hot-pressed sample of EuO are presented for the temperature range 50–300 °K. A sharp minimum occurs in the thermal conductivity near the temperature of the paramagnetic-ferromagnetic transition, 69 °K. Behavior of K at low temperatures and near the magnetic critical temperature is discussed for magnetic solids.

I. Introduction

Compounds of divalent europium with oxygen, sulfur, selenium and tellurium have the NaCl structure and exhibit magnetic ordering below a critical temperature T_c, with the europium ion in the $^8S_{7/2}$ spin configuration [1–5]. EuO and EuS are ferromagnetic and EuSe [6] and EuTe are antiferromagnetic. The critical temperatures T_c as determined from sharp upwards peaks in plots of specific heat *vs* temperature for EuO, EuS, EuSe and EuTe are reported to be 69.3 °K [7, 8], 16.3 °K [9], 4.6 °K [9] and 9.6 °K [9]. Although EuO was the first member of the family to be studied most experimental and theoretical work seems to have been centered on EuS [10–18]. Busch and co-workers in Zurich have studied these and similar compounds since 1962 [1, 2, 9, 20–26]. We report measurements of the thermal conductivity of EuO in the temperature range $T = 50$–300 °K.

II. Experimental

The sample used in this study was a hot-pressed rod 2.9 mm in diameter and 19 mm long. It was supplied by Semi-Elements, Inc.[3]), who specified that it consisted of at least 90% EuO and the remaining Eu_2O_3. We used the linear absolute method with a guarded radiation shield. Three copper-constantan thermocouples were used to measure temperature gradients; the temperature of the cryogenic bath was monitored with a platinum resistance thermometer and that of the heat sink with a germanium resistance thermometer. Plots of the gradient-heater power *vs* temperature gradient were drawn for each temperature, and the thermal conductivity for that temperature was obtained from the slope. A test run with Armco iron as the sample gave results within 6% of published values [27].

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III. Results

Results for two different mountings of the same sample are shown in Figure 1. The value of K is seen to fall off by about a factor of four as the temperature goes

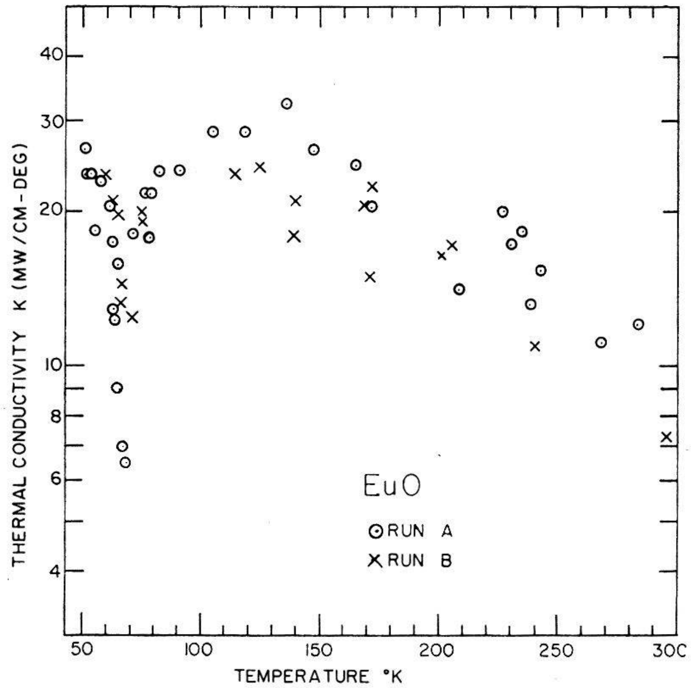

Figure 1

Thermal conductivity K of EuO as a function of the absolute temperature T. EuO is ferromagnetic below 69 °K and paramagnetic above. A sharp minimum in K occurs at 69 °K.

below 100 °K, and to rise again by about 55 °K. The center of the minimum is at 69 °K. The position of this minimum gives an independent determination of the critical temperature at which ferromagnetic ordering occurs.

IV. Discussion

1. *Critical Temperature T_c*

The critical temperature T_c of EuO has been determined previously as 69.3 °K from specific heat measurements [7, 8] and more recently as 69.2 °K from measurements of the thermal expansion anomaly [28]. Our measurements give 69 °K.

2. *Shape of Curve*

The general shape of the thermal conductivity curve, with a dip at the critical temperature, has been observed in a number of other materials. The thermal conductivity of some of these is plotted in Figure 2. EuO is shown for comparison. Ferromagnetic cobalt has not been measured above 430 °K; its Curie point is 1393 °K. Several materials which exhibit anomalies in K at T_c are listed in Table I.

3. *Spin System*

Ordering of spins in a magnetic solid may affect the thermal conductivity two ways. First, spin-wave excitations set up in these ordered spins can provide an additional heat transport mechanism. Second, the ordered spins are not as effective in reducing lattice conductivity as are the disordered spins. This latter effect probably gives rise to the break in the slope of K *vs* T at T_c, with the slope more positive on the high-temperature side. A magnetic field applied to the material will both increase the ordering and suppress the spin waves. Hence it will increase the conduction by the lattice and decrease the conduction by the spin waves.

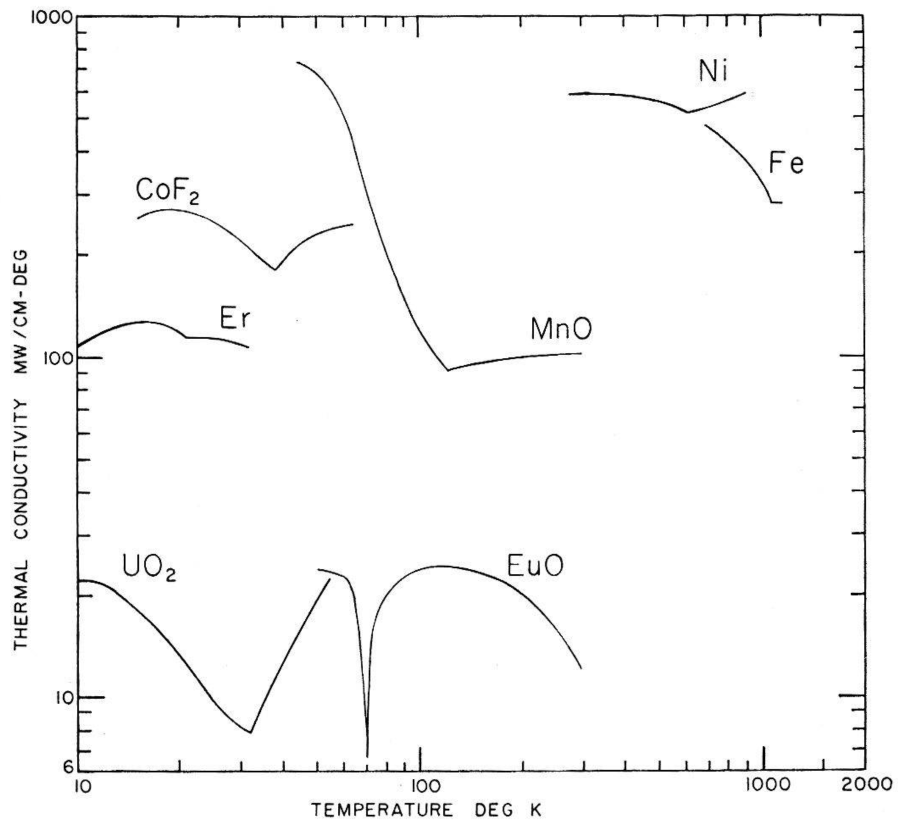

Figure 2

Anomalous behavior of thermal conductivity of several magnetic solids near the critical temperature. Results for EuO are included for comparison. The type of magnetic transition and the critical temperature are given in Table I.

Spin waves provide appreciable heat flow only at a very low temperature. Thus one needs to account for the spins as scatterers more often than as carriers. Although the specific heat of magnetic solids usually exhibits a well-known spike upward at T_c [7–9], the thermal conductivity rarely, if ever, exhibits such an upwards spike because the conductivity associated with the spin excitations (proportional to the magnetic part of the specific heat) is usually small with respect to the lattice conductivity except at the lowest temperatures, and so it is small at the critical temperature. We do not associate spin-wave conductivity with the anomaly observed in EuO.

Spin-wave conductivity has been described by Sato [49] and by Douthett and Friedberg [50]. Thermal conductivity varies as T^2 and is reduced by application of a magnetic field. Excellent agreement with theory has been obtained by Lüthi [51], by Douglass [52] and by Friedberg and Harris [53] measuring yttrium iron garnet (YIG), $Y_3Fe_5O_{12}$, and by McCollum et al. [16] measuring EuS.

Table I

Some materials with anomalous behavior of thermal conductivity K at the critical temperature T_c

Material	T_c (°K)[a]	Behavior of K at T_c[b]	Reference
Fe	$T_{F-P} = 1043$	minimum	[27]
Ni	$T_{F-P} = 633$	minimum	[29, 30]
Sm	$T_{A-P} = 106$	slope increase	[31, 32]
Gd	$T_{F-A} = 230$	minimum	[33, 34, 35]
	$T_{A-P} = 270$	slope increase	
Tb	$T_{A-P} = 235$	minimum	[36, 34, 35]
Dy	$T_{F-A} = 85$	slope increase	[37, 35]
	$T_{A-P} = 180$	minimum	
Ho	$T_{F-A} = 19$	minimum	[38]
Er	$T_{F-A} = 19$	minimum	[39, 38]
Tm	$T_{A-P} = 57$	minimum	[66]
Yttrium-calcium iron garnets	$T_{A-P} =$ 112–553	minimum	[40]
MnTe	$T_{A-P} = 307$	slope increase	[41]
UO_2	$T_{A-P} = 31$	deep, wide minimum	[42, 43]
CoF_2	$T_{A-P} = 38$	minimum	[44]
MnO	$T_{A-P} = 120$	minimum	[45]
MnF	$T_{A-P} = 67$	slope increase	[44]
CoO	$T_{A-P} = 290$	slope increase	[46]
$CuCl_2$	$T_{A-P} = 4.33$	decrease in mean free path near T_c	[47]
$CoCl_2$	$T_{A-P} = 2.28$	decrease in mean free path near T_c	[47]
EuO	$T_{F-P} = 69$	minimum	[48]

a) $F-P$ means ferromagnetic-paramagnetic transition; $A-P$ means antiferromagnetic-paramagnetic transition; $F-A$ means ferromagnetic-antiferromagnetic transition.

b) *Slope increase* implies dK/dT greater for $T > T_c$. *Minimum* implies deep minimum, broad minimum, or inflection point.

A masking of the spin-wave conductivity may occur because of impurities, the phonon contribution to K, and the spin-phonon interaction. Also, as the spin waves are suppressed by the application of a magnetic field, spin-phonon scattering will *decrease* and the phonon conductivity will *increase*. This increase may obscure or even outweigh the corresponding decrease in K due to the spin waves.

4. *The Spin-phonon Interaction*

The spin-phonon interaction generally reduces K in magnetic solids and it has been treated by several authors [54–57]. Bhandari and Verma [57] have been more successful in describing K for YIG to higher temperatures (20 °K) than earlier authors by taking this interaction into account. Nettleton [55] has attempted to fit data on MnF_2, CoF_2 and MnO; spin-phonon and point-defect scattering dominated the thermal resistivity $1/K$ at temperatures below that of the maximum in K. Joshi [56] used

Nettleton's approach on both YIG and $MnFe_2O_4$. The spin-phonon interaction is the probable cause for the dip in thermal conductivity of EuO near T_c.

5. *Near the Critical Temperature*

KAWASAKI [58] studied thermal conductivity near T_c in insulators for $T_c \ll \theta$, the Debye temperature. He started with the correlation function expression for K, verified that the spin-wave conductivity would indeed be negligible near T_c, and at least qualitatively explained the dip in K at T_c in terms of critical scattering of phonons by critical fluctuations in the energy density of the spin system. STERN [59] has treated the problem in a manner similar to Kawasaki.

As the critical temperature is approached from above one may think of these critical fluctuations as being regions of spin alignment both increasing in size and lasting for longer periods of time. At $T = T_c$ one region is infinite in extent and lasts for an infinite time. Because the energy densities are revealed in the specific heat of the spins (to use Kawasaki's phrase), an upward peak in the specific heat will be associated with a downward dip in the thermal conductivity. We believe this is qualitatively the reason for the behavior of K in EuO.

6. *Phase Transitions*

The magnetic phase transition from one type of order to another, or to disorder, is usually considered to be a second-order phase transition – one in which there is a discontinuity in the second derivative of the free energy (but none in the first derivative and hence no latent heat). A general discussion of equilibrium physical properties at phase transitions is given by FISHER [60]. Properties such as specific heat and susceptibility are often expressed in terms of $|T - T_c|^{-a}$ near T_c. No critical exponent, as a is called, seems to have been worked out for nonequilibrium properties such as thermal conductivity except for liquid helium, where $K \propto |T - T_c|^{-1/3}$ for $T > T_c$, the lambda point [61]. For the somewhat closely related ultrasonic attenuation, TANI and MORI [62] derive a dependence of $(T - T_c)^{-1}$, and PAPOULAR [63], one of $(T - T_c)^{-1/2}$. HUBER [64] has taken a step toward relating thermal conductivity to ultrasonic attenuation near T_c by pointing out that KAWASAKI's [58] theory and that of TANI and MORI [62] are in harmony if the thermal conductivity of the magnetic lattice is singular at the transition temperature.

In the present work we plotted $1/K$ *vs* T and assumed

$$1/K = (1/K)_g + (1/K)_m ,$$

where $(1/K)_g$ is the lattice resistivity equal to the extrapolated value across the anomaly and $(1/K)_m$ is the magnetic resistivity responsible for the anomaly. The temperature dependence of $(1/K)_m$ so determined is given below:

$$T < T_c:\ (1/K)_m \propto (T_c - T)^{-a'},\ 1 < a' < 3/2 ,$$
$$T > T_c:\ (1/K)_m \propto (T - T_c)^{-a},\ 1/2 < a < 3/4 .$$

These power law behaviors are similar to those discussed for ultrasonic attenuation in a Heisenberg paramagnet [62, 63, 65].

V. Conclusions

The sharpness and location of the experimental dip in K at T_c for EuO definitely suggest an inverse dependence on and close relationship with the corresponding rapid change in the specific heat. Kawasaki offers a qualitative understanding of the dependence and relationship, which apparently occur in several materials: critical fluctuations in the spin system energy density are extremely effective phonon scatterers near the critical temperature. The temperature dependence of the magnetic part of $1/K$ is consistent with derivations of the temperature dependence of ultrasonic attenuation.

Acknowledgement

The authors are grateful for an exchange of letters with Prof. D. L. Huber and for many illuminating discussions with Prof. J. D. Patterson.

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