

TRANSPORT PROPERTIES IN FERROMAGNETIC RARE EARTH ALLOYS (Tb-Gd) AND TbZn COMPOUND (*) (**)

J. B. SOUSA, R. S. PINTO, M. M. AMADO

J. M. MOREIRA, M. E. BRAGA

Centro de Física da Universidade do Porto, Porto, Portugal

M. AUSLOOS

Int. Centre Theor. Sol. St. Phys. ESIS, Univ. Liège B5, Liège, Belgium

D. HUKIN

Clarendon Laboratory, Univ. Oxford, Parks Road, Oxford, England

ABSTRACT—Very accurate data on the thermoelectric power (S) and the temperature derivative dS/dT have been obtained for a set of poly- and mono-crystalline ferromagnetic Tb-Gd alloys (80–340 K). The critical behaviour of S and dS/dT in the vicinity of the Curie point is analysed in detail; direct comparison is made with the critical behaviour of the electrical resistivity (ρ , $d\rho/dT$).

The critical behaviour of the thermal conductivity (k) near a magnetic phase transition (T_c) is also considered, and a new method to obtain very accurate data near T_c is discussed ($1:10^4$ resolution). Preliminary results are presented for a single crystal of ferromagnetic TbZn.

1 — INTRODUCTION

The theory of the variation of $d\rho/dT$ near the Curie temperature of magnetic metals has been presented by several authors and refined recently [1]. In particular, the qualitative features of $d\rho/dT$ close to T_c are essentially determined by the magnitude of the parameter $k_F d$, where d is the relevant lattice parameter [2]. For low $k_F d$ values, the usual maximum in $d\rho/dT$ at T_c should be immediately

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followed by a sharp negative minimum, just above T_c . For high $k_F d$ values, the predicted minimum is much attenuated and should occur only at $T \gg T_c$, where the high phonon background in $d\rho/dT$ probably overshadows that feature (Ni-like behaviour).

Our knowledge on transport properties such as the thermoelectric power (S , dS/dT) and the thermal conductivity (K , dK/dT) is rather limited. This comes mainly from the greater complexities inherent in the theoretical treatments of both properties, and from the well known experimental difficulties involved in the *accurate* determination of S and K , as is required for critical phenomena studies. Some relevant literature is given here for the thermoelectric power [3–23] and the thermal conductivity [3, 24–29].

By using a very anisotropic rare-earth binary system (Tb-Gd, hexagonal structure), and by measuring $d\rho/dT$ along a and c axes ($k_{F_c} c \ll k_{F_a} a$) we have made recently the experimental confirmation of the theoretical predictions on the effect of the $k_F d$ parameter in $d\rho/dT$ [30]. In this preliminary report we extend the information on this system to the case of the thermoelectric power (S) and its temperature derivative (dS/dT).

As for the thermal conductivity, we present here a new experimental approach to obtain direct information on the *changes* of the thermal conductivity near a magnetic critical point. A preliminary set of results is given for the case of the thermal conductivity of a monocrystalline ferromagnetic sample of TbZn near its critical point.

2 — EXPERIMENTAL TECHNIQUES

2.1 — Thermoelectric power

The thermoelectric power was obtained with a static method. The temperature difference across the sample ($\Delta T \approx 0.5$ K) was measured with a differential copper/constantan thermocouple, in good contact with (but electrically insulated from) the sample. Another similar thermocouple (T) allowed the determination of the sample mean temperature. The thermoelectric voltage (ΔV) was measured using Cu leads spotwelded to the sample. Both thermocouple and thermoelectric voltages were measured directly on sensitive digital voltmeters, with 10^{-2} μ V resolution. Further details of the method can be found elsewhere [33].

2.2 — Thermal conductivity

It is well known that the accurate measurement of the thermal conductivity puts serious experimental difficulties. Standard accuracy is of the order of 1%, but in some exceptional cases accuracies of ~0.1% have been achieved. In this context, it is instructive to compare the intrinsic difficulties inherent to thermal conductivity, thermoelectric power and electrical resistivity measurements.

By far electrical resistivity measurements are the easiest and the most accurate, enabling relative resolutions in ρ as high as 1 part in 10^7 . The reason is that, apart from a geometrical factor, the resistivity measurements essentially involve only the accurate measurement of electrical voltages (V). Assuming as typical $V \sim 10^3 \mu\text{V}$, and a nanovolt detection level, we achieve easily $1/10^6$ in resolution.

In a thermoelectric power measurement ($S = \Delta V / \Delta T$), besides an electrical voltage $\Delta V (= S \cdot \Delta T)$, we must also measure the small difference of temperature ΔT . Assuming the use of a differential thermocouple to measure ΔT , this is equivalent to a voltage measurement $\Delta V_o (= S_o \cdot \Delta T)$, where S_o stands for the sensitivity of the thermocouple. Since one always aims at the highest possible value for S_o , we generally have $S_o \gg S$, $\Delta V_o \gg \Delta V$. Therefore, problems in voltage measurements tend to arise first in ΔV . Assuming $S \sim 4 \mu\text{V K}^{-1}$, $\Delta T \approx 0.5 \text{K}$, we are faced with the accurate measurement of a small voltage $\Delta V \approx 2 \mu\text{V}$. Even with nanovolt resolution, and neglecting all other causes of error, we could not expect better than $5/10^4$ resolution when a difference $\Delta T \approx 0.5 \text{K}$ is used.

In a thermal conductivity measurement ($K = f\dot{Q}/\Delta T$), apart from a geometrical factor f , we must measure ΔT (equivalent to an electric voltage) and the heat flow \dot{Q} inside the sample. This last measurement involves the accurate estimate of all the heat losses from the sample, which are far from negligible in every case. This explains the difficulties in achieving even 0.1% resolution in thermal conductivity measurements.

Let us consider now the special case of critical phenomena, for which very accurate and detailed data are usually required down to 10^{-4} (or better) of the critical point. In spite of these severe demands, nature is sometimes generous to those properties which cannot be measured with the highest accuracy. For example, the relative chan-

ges produced by a magnetic phase transition in the thermoelectric power are usually much bigger than the corresponding ones for the electrical resistivity. For instance, in TbZn near T_c we have $(1/\rho) (d\rho/dT) \sim 5 \cdot 10^{-3}$, whereas $(1/S) (dS/dT) \sim 10^{-1}$. Unfortunately, the same does not happen with the thermal conductivity.

Still, some progress can be made here if we remember that the important features in critical phenomena do occur in a very restricted range of temperature, within which the non-critical contributions can hardly change significantly.

Even not being able to measure accurately the crucial quantity \dot{Q} , it might be possible to maintain it practically *constant* over a very restricted range of temperature, if one uses a relatively short period of time to bridge it. Then $K \approx \text{const.} (\Delta T)^{-1}$, and the relative changes in K are simply equal to the relative changes in ΔT :

$$\frac{1}{K} \frac{dK}{dT} \approx \frac{1}{\Delta T} \frac{d(\Delta T)}{dT}$$

Let us examine in more detail the validity of this approximation, starting from \dot{Q} . This is simply given by the difference between the power dissipated in the sample heater (\dot{Q}_o) and the heat losses (\dot{q}). Using a very stable current and heater winding, it will not be difficult to maintain \dot{Q}_o practically constant over a limited range of temperature.

As to the heat losses \dot{q} , which are usually a small (although non-negligible) fraction of \dot{Q} , the important point is that they essentially depend on the difference of temperature between sample and surroundings. Assuming, in first approximation, that \dot{q} is proportional to some small power α of ΔT , and taking f and \dot{Q}_o as constants, we can easily show that :

$$\frac{1}{K} \frac{dK}{dT} = \frac{1}{\Delta T} \frac{d(\Delta T)}{dT} \left[1 + \alpha \frac{\dot{q}}{\dot{Q}_o} \right]$$

Therefore, if we keep $\dot{q} \ll \dot{Q}_o$, the relative changes in the thermal conductivity are approximately equal to the corresponding changes in ΔT . This procedure, which only requires the accurate measurement of ΔT , has been used here to investigate the relative changes in the thermal conductivity of TbZn through its magnetic-structural phase transition in the vicinity of 200 K.

3 — THERMOPOWER IN Tb-Gd ALLOYS

3.1 — Experimental results

Fig. 1 shows the thermoelectric power S of a polycrystalline ferromagnetic sample of $Tb_{75}Gd_{25}$, measured in increasing temperatures from 80 to 340 K. The critical temperature ($T_c \approx 244$ K), as obtained from electrical resistivity measurements ($d\rho/dT$) [30] is also marked on the graph.

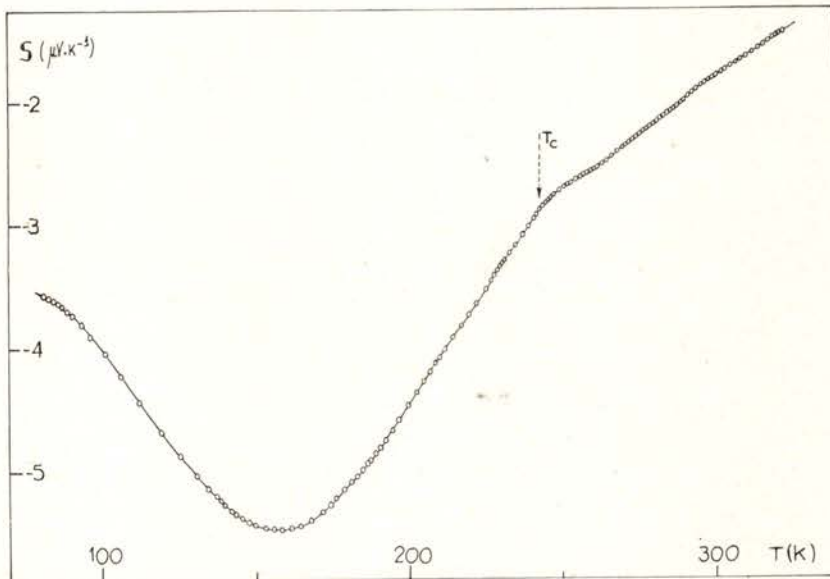


Fig. 1 — Temperature dependence of thermoelectric power (S) in polycrystalline $Tb_{75}Gd_{25}$; T_c is the Curie temperature.

The *general* features of $S(T)$, including its magnitude and sign, closely resemble those found in the basal thermoelectric power of pure monocrystalline Terbium [7]. The pronounced minimum in S is still present around 160 K, and the ferro-paramagnetic transition is also accompanied by a pronounced decrease in the slope of the curve when the sample enters the paramagnetic state.

The same qualitative features at the magnetic transition are also found in the electrical resistivity, as shown in fig. 2. The resemblance

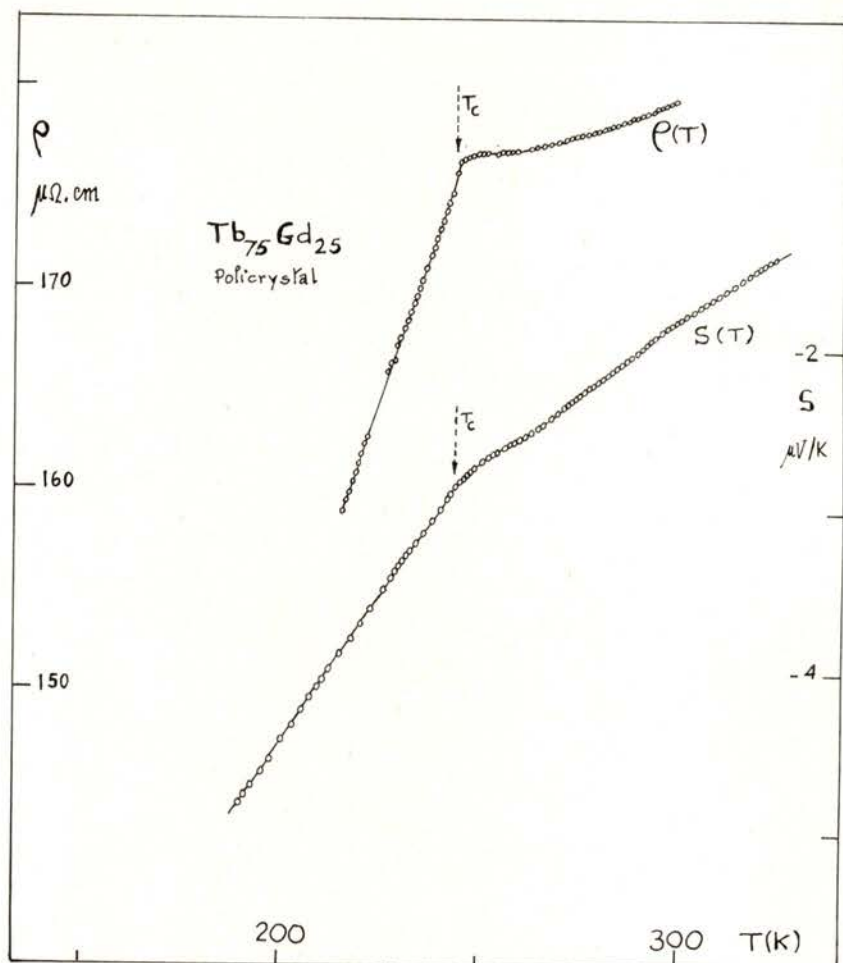


Fig. 2 — Thermoelectric power (S) and electrical resistivity (ρ) for $Tb_{75}Gd_{25}$ polycrystalline sample.

between the behaviour of the thermoelectric power and the electrical resistivity becomes more evident when we compare the temperature derivatives $d\rho/dT$ and dS/dT (fig. 3).

We also measured the thermoelectric power in a *monocrystalline* sample of $Tb_{75}Gd_{25}$, with the temperature gradient applied along the c-axis. The behaviour is now very different from that found in the polycrystalline sample, S exhibiting a pronounced hump below T_c and an absolute maximum around $T=145$ K, as shown in

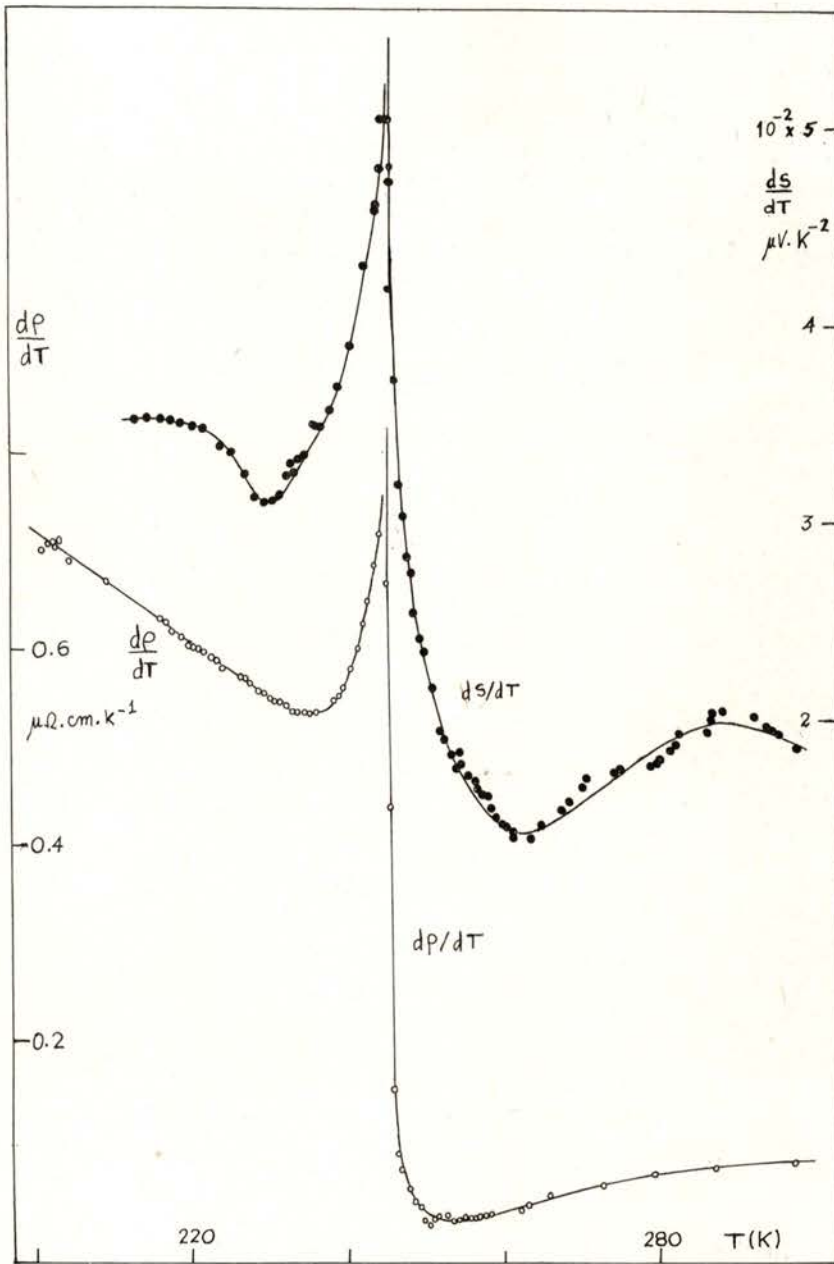


Fig. 3 — Critical behaviour of the temperature derivatives dS/dT and $d\rho/dT$ for polycrystalline $\text{Tb}_{75}\text{-Gd}_{25}$ sample.

Fig. 4. A similar hump below T_c has been found in the c -axis thermoelectric power of other ferromagnetic heavy rare earth metals like Gd and Tb [6].

The ferro-paramagnetic transition for this monocrystalline sample of Tb-Gd is again associated with a change in the slope of the $S(T)$ curve in the vicinity of $T_c = 244$ K. However, due to the steepness of the $S(T)$ curve in this region, it is difficult to extract further information on the dS/dT details within the critical region.

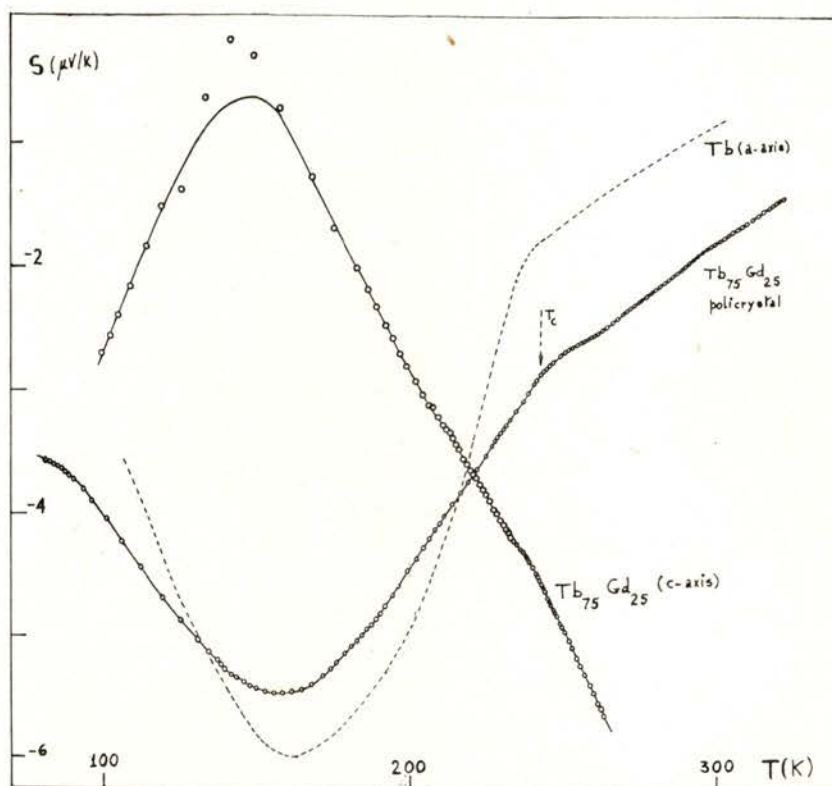


Fig. 4— $S(T)$: Tb₇₅-Gd₂₅ single crystal along c -axis; Tb (a -axis); Tb₇₅-Gd₂₅ (polycrystal).

In the same figure, a direct comparison is made between our S results for poly- and monocrystalline (c -axis) Tb₇₅-Gd₂₅ samples and those for the basal (a -axis) thermoelectric power of pure Tb. The radical differences between the a - and c -axis behaviour should be appre-

ciated. This pronounced anisotropy in $S(T)$ is in contrast with the relatively small anisotropy of the electrical resistivity curves $\rho(T)$ in the ferromagnetic region [25]. We should also stress the large *negative* slope of S in the paramagnetic region for the c -axis $\text{Tb}_{75}\text{-Gd}_{25}$ sample, as compared with the *positive* slopes found in the polycrystalline sample, and in the a -axis thermoelectric power of pure Tb.

3.2 — Discussion

As pointed above, the thermoelectric power for the polycrystalline $\text{Tb}_{75}\text{-Gd}_{25}$ sample exhibits a behaviour which closely resembles the one found for the electrical resistivity in the vicinity of the critical point. These similarities have also been found in other ferromagnetic systems, e.g. in Ni and Gd [5] and GdNi_2 [8]. For antiferromagnets, the same intimate connection between $d\rho/dT$ and dS/dT has been observed by Fote *et al* [4] in their detailed and very accurate thermopower measurements in pure chromium. Recently we have shown [31] for an antiferromagnetic $\text{Cr}_{99.94}\text{Al}_{0.06}$ alloy that $d\rho/dT$ and dS/dT accurately obey a linear relation, both above and *below* T_N . This strongly suggests that both properties are governed by the same critical exponents in the transition region. However, further experiments are still needed, particularly in the range of reduced temperatures down to $\varepsilon \approx 10^{-4} - 10^{-5}$, in order to see if these findings still hold in the *very vicinity* of T_N .

The general features of S below T_c are qualitatively consistent with Kasuya's predictions for the ferromagnetic region [3]. The pronounced rise in S with increasing temperature in the ferromagnetic region is due to the increasing magnetic-spin disorder in the system. However, the rate of increase of S with T slows down as we approach T_c , giving a shallow minimum in dS/dT , as we see in Fig. 3. A similar decrease of dS/dT has also been observed in the basal thermoelectric power of pure Gd [5].

In the paramagnetic region there is a minimum in dS/dT at temperatures slightly above T_c , in the same manner as for $d\rho/dT$ in the same sample. As shown elsewhere [30], this minimum is reminiscent of that found along the c -axis, and such c -axis effects are always present (in some degree) in a polycrystalline sample.

We have not yet measured the thermoelectric power of $\text{Tb}_{75}\text{-Gd}_{25}$ along a basal axis. Let us then consider the case of the thermoelectric

power along the c -axis in the $\text{Tb}_{75}\text{-Gd}_{25}$ monocrystal. For this direction the general behaviour of S is very anomalous, showing a pronounced hump below T_c , as also happens in other ferromagnetic rare earth metals like Gd [7]. Apparently similar humps below the critical temperature are also present in antiferromagnetic metals, where they can be explained in terms of the appearance of an energy gap in the electron spectrum due to the extra periodicity caused by the spatially modulated antiferromagnetic structure. Obviously, no such explanation can be advanced for a ferromagnetic system.

Legvold [7] relates the humps below T_c in ferromagnetic rare earth metals to the effect of the internal field, which shifts the conduction band into spin-up and spin-down bands. This means that there will be Fermi surface effects which should show up in the thermoelectric power. On the other hand, Tang *et al* [5] argue that it is possible to reconcile the a - and c -axis thermoelectric power of Gd by ascribing the humpback anomaly to the effect of anomalous negative lattice expansion along the c -axis of Gd.

For this monocrystalline c -axis $\text{Tb}_{75}\text{-Gd}_{25}$ sample, we were not able to extract accurate data on dS/dT to enable a relevant comparison with $d\rho/dT$. We observe, however, that dS/dT gets more negative with the transition to the paramagnetic phase, as also happens with $d\rho/dT$, for which a sharp negative minimum is observed just above T_c .

Work is in progress for the measurement of the thermoelectric power and its temperature derivative in the vicinity of the critical point in other monocrystalline Tb-Gd samples.

4 — THERMAL CONDUCTIVITY IN TbZn

4.1 — *Experimental results*

When using the method described in 2. over a restricted range of temperatures and with \dot{q}_0 approximately constant and fairly small, the thermal conductivity is approximately proportional to the inverse of the temperature difference (ΔT) across the sample.

Vacuum conditions in the experimental chamber were 10^{-6} torr, and a temperature rate of 20 mK/minute was used during the measurements. As a compromise between accuracy and detail we adopted $\Delta T \approx 1$ K.

Fig. 5 shows, apart from a constant factor, the inverse of ΔT as a function of temperature for a ferromagnetic monocrystalline sample of TbZn, which is a compound with CsCl structure and a critical temperature $T_c \approx 200$ K [32]. Our results span the temperature interval from 180 to 210 K. In contrast to the case of the thermoelectric power of TbZn, the K -variation is rather weak over the range

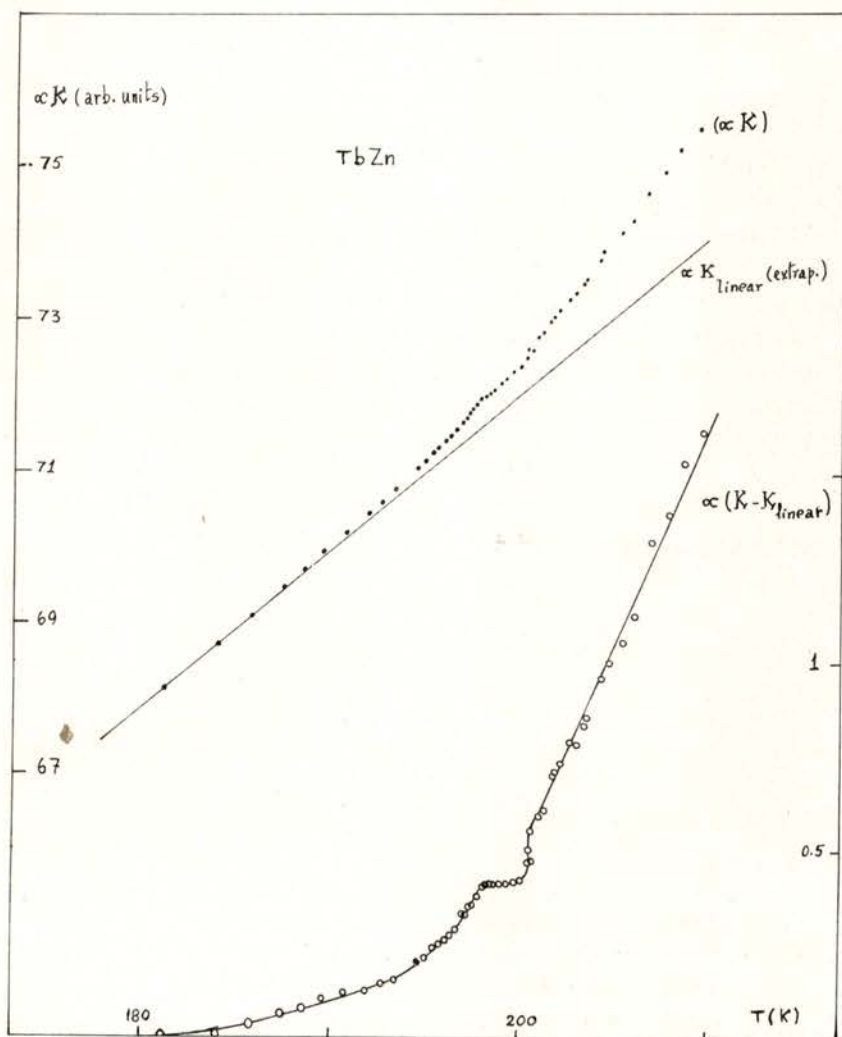


Fig. 5 — Upper curve: Thermal conductivity for single crystal of ferromagnetic TbZn (k_{lin} = linear extrapolation from low temperature data).

Lower curve: $(k - k_{lin})$ shows clearly the anomaly near the Curie temperature.

of temperatures investigated ($K^{-1} dK/dT \sim 10^{-3}$ as compared to $S^{-1} dS/dT \sim 10^{-1}$ Kelvin $^{-1}$).

Away from the transition region, K shows an almost linear dependence on T , but with a different magnitude in the (positive) slopes below and above T_c . In particular, the thermal conductivity increases with T at a much bigger rate in the paramagnetic region. This is in contrast with the monotonic decrease of the thermal conductivity in the case of ordinary metals, towards an approximately constant value at high temperatures. We observe however that positive dK/dT values in the paramagnetic phase have also been observed in pure Tb, Ho and Gd, both along a - and c -axes [25].

In order to get further insight into the details of the thermal conductivity in the transition region, we subtracted from $K(T)$ a linear background, as also shown in Fig. 5. We see that K increases very rapidly with T as we approach the critical region from below, showing a well marked kink between ~ 198 and 199 K.

In the critical region K has a very complex behaviour, and we cannot exclude the possibility of an almost discontinuous step in K at a temperature fairly close to 200 K. On the whole, it generally looks as if the critical fluctuations cause a depression on the thermal conductivity below its general trend in the neighbourhood of the critical region. In the paramagnetic region, the marked increase in dK/dT should be emphasized again.

4.2 — Discussion

The scarce experimental information generally available on the thermal conductivity, and the fairly small changes which occur near T_c , preclude at the present stage of our knowledge, any discussions on such matters as the values for the critical exponents of dK/dT within the critical region. Therefore, only the general features of the thermal conductivity will be considered here.

The sharp increase of the slope dK/dT in the paramagnetic state can be easily understood in terms of an enhancement in the electron scattering, due to the spin-disorder in the paramagnetic phase. Qualitatively, we can describe this effect in terms of a modified Wiedemann-Franz law, since previous measurements in Tb [25] show that $K\rho/T$ keeps a fairly constant value ($L \neq L_0$, Lorentz number) in the first part of the paramagnetic region, with a particular

(constant) value for each crystal orientation. Assuming this, we should have for the thermal conductivity,

$$K = L \cdot T \cdot \frac{1}{\rho_o + \alpha T + \rho_s}$$

where ρ_o is the (constant) impurity resistivity, αT is the phonon contribution to the electrical resistivity, and ρ_s is the spin-disorder resistivity, which is constant in the paramagnetic phase. In magnetic metals at ordinary temperatures, the spin-disorder dominates the phonon-term, and we should have

$$K \simeq \frac{L}{\rho_o + \rho_s} \cdot T$$

i.e. a linear increase of K with T , in good agreement with experiment. In the ferromagnetic phase, magnetic order increases, which decreases the electron-spin scattering, lowering therefore ρ_s . In particular ρ_s can get smaller than αT , and for reasonably pure materials we should then have

$$K \simeq L/\alpha$$

which gives a zero slope for the thermal conductivity curve.

Finally, let us consider the behaviour of K near $T_c \simeq 200$ K. Here, we can say that the thermal conductivity appears depressed with respect to the extrapolated behaviour from both sides of the critical region. It therefore suggests the existence of extra scattering mechanisms for the heat carriers in the system (electrons, magnons and phonons). We think that phonons might play a relevant role, since the magnetic transition in TbZn at 200 K is accompanied by a structural transition, from a tetragonal ($T < T_c$) to a cubic lattice structure ($T > T_c$).

Since the phonon spectrum is directly affected by any alteration in the atomic spacing, and above all by a change in symmetry, we should not rule out the possibility of such an explanation for the almost discontinuous increase in K at temperatures slightly above 200 K.

Further work is still needed to clarify this interesting behaviour of K near a magnetic-and-structural phase transition. We are certainly

aware of the great experimental difficulties ahead, and also that we are almost in the limit of potentialities in our present techniques.

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