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EFFECTS OF THE NÉEL TRANSITION ON THE THERMAL AND ELECTRICAL RESISTIVITIES OF Cr AND Cr:Mo ALLOYS

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Thermal conductivity enhancements due to magnetic phase transitions have been observed for chromium, chromium-molybdenum alloys, and several rare-earth metals. The phenomenon can thus no longer be considered an uncommon one in metallic systems. In chromium, it appears to be sensitive to the microscopic state of particular samples.

In a previous Letter[1] we presented evidence for an enhancement of the thermal conductivity of chromium in the vicinity of its Néel point T_N. It was suggested that the thermal-conductivity increase and corresponding Lorenz-number increase were related to the growth of critical fluctuations of the energy density of the spin-density-wave system. Because chromium is antiferromagnetic there also occurs magnetic superzone boundary scattering, and this is primarily responsible for the characteristic hump-backed part of the electrical resistivity curve below T_N. When the superzone resistivity is combined with the phonon and fluctuation resistivity contributions, there results a resistivity minimum close to T_N. A study of the experimental results led us to consider that superzone boundary scattering affects the thermal resistivity, too. This work has now been extended by investigating the temperature dependence of the thermal and electrical conductivities of dilute chromium alloys. The homologous element molybdenum was deemed a suitable solute because its presence is known to lower T_N and to raise rapidly the electrical resistivity in the antiferromagnetic state.[2] At the same time we wished to study the lattice contribution to the thermal conductivity and also to resolve the effects of band structure on the electronic contribution. A detailed discussion of these latter problems will be published elsewhere. The present results on chromium alloys have facilitated, for both the thermal and electrical resistivities, separation of the critical scattering from other scattering effects, and have permitted independent substantiation of the results of the previous Letter on chromium. In addition, the original chromium sample has been well annealed and remeasured, and the new data confirm the correctness of the earlier work for the sample investigated. Since we have also observed thermal-conductivity enhancements at magnetic critical points in terbium and holmium single crystals[3] and others have reported thermal-conductivity or Lorenz-number peaks at magnetic critical points in other rare-earth metals,[4-7] we conclude that the effects reported in the present Letter for chromium and its alloys have a wider generality than hitherto supposed. We should also say that besides the intrinsic importance of the new results reported herein, they are also of significance in view of two other recent Letters to this journal.[8,9] These references will be referred to as MWM and LM, respectively.

Our method for determining the thermal conductivity $\lambda(T)$ was, as before, that of longitudinal heat flow using Au-0.03 at.% Fe against chromel-*P* for the differential thermocouple thermometry. Probe separation for the various samples was 3 to 4 cm and the temperature differences lay in the range 0.2 to 0.3°K over this length. The output from this differential thermocouple was detected by a Honeywell centimicrovolt potentiometer, type 2779, in conjuction with a Guildline galvanometer-amplifier system. This permitted a voltage drift of 1 nV during the course of an hour to be discerned. Prior to our first chromium measurements,[1] test experiments were carried out on high-purity silver and copper.[10] The choice of silver is apt because the thermal conductivity varies little with temperature between 150 and 300 K.[11] Our results agreed well, as regards both temperature dependence and absolute magnitude, with the best data in the literature.[11,12]

The previously studied chromium sample[1] was annealed in a vacuum of better than 10^{-6} Torr for 75 h above 1000°C of which 50 h were passed at 1200°C. This led to grain growth with the largest grains 2-4 mm in diameter, and produced a residual resistivity ratio (RRR) of 295. This value is higher than those for MWM's samples A and B,[8,13] although not as high as that of their sample A after annealing (380).[9] The electrical and thermal resistivities between 280 and 330 K are provided in Fig. 1. The behavior of the Lorenz number $L(T)$ in the critical region is indicated, too. Inserted into this figure, in order to aid comparison with previous work, are two insets: inset (a) which shows $L(T)$ for the chromium sample before annealing, together with MWM's and LM's results on their own samples; and inset (b) which shows $\rho(T)$ and $W(T)$ for our chromium sample before annealing.

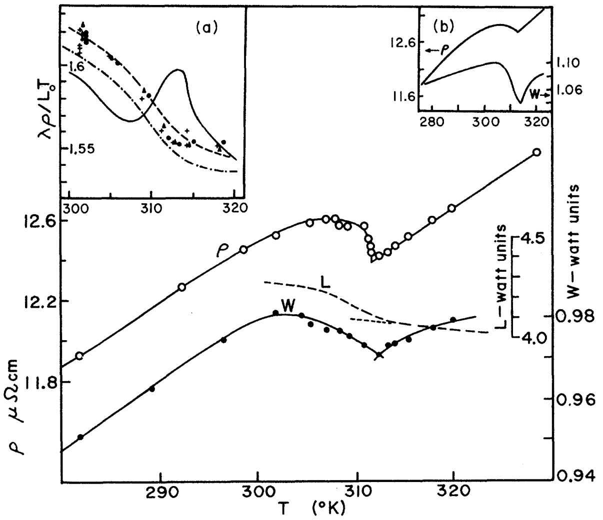

FIG. 1. Thermal and electrical resistivities of annealed chromium (RRR 295) between 280 and 320 K. The Lorenz function $L(\equiv \lambda\rho/T)$ in the Néel transition region is indicated by the broken line. Inset (a): The ratio $\lambda\rho/L_0T$ for chromium, where L_0 is the Sommerfeld value of the Lorenz number. Solid line: Results on unannealed chromium, RRR 178 (Ref. 1). Dash-dotted line: Results on chromium sample B of Ref. 13 (RRR 58). Dashed line: Results on chromium sample A of Refs. 13 and 8 (MWM) (RRR 280). Dots, circles, and crosses: Results on chromium sample A of Ref. 9 (LM) (RRR 380). Inset (b): Thermal and electrical resistivities of our chromium before annealing (RRR 178; Ref. 1)

Considering first the electrical resistivity, the magnetic superzone scattering contribution is responsible for the main anomaly below T_N. At ρ_{max} (308 K) the electrical resistivity has a value which is nearly 3% higher than if chromium had remained paramagnetic on cooling. Rather similar features are displayed by the temperature variation of the thermal resistivity. A minimum is located at 312 K, whereas before annealing it was at 313.5 K. For the electrical resistivity ρ_{min} is at 311.7 K compared with 312.2 K before annealing. Regarding the depression of the thermal resistivity, or the enhancement of the thermal conductivity, in the region of the Néel point, it is clear that the effect is not as strong as it was before annealing. If, for simplicity, the anomaly is defined with respect to the difference $W_{max}(303)-W_{min}(312)$ its magnitude appears as 1.2%, compared with 6% prior to annealing.[14] The transport processes in the vicinity of the Néel point therefore appear to be acutely sensitive to the microscopic state of the sample. Moreover, the fact that different samples, although of high purity and having fairly similar residual resistivity ratios, behave so differently over this particular temperature region indicates that the basic interactions responsible for the effect in this complex electron-phonon coupled system are subtle ones. Since the temperature region concerned is the one where critical fluctuations predominate, it is probable that their presence, together with perhaps changing domain patterns modified by different grain dimensions, impurity atom distributions, and strain regions, are ultimately responsible.

At this juncture we point out that, while below 300 K MWM find that, as for our sample, the thermal resistivity of their sample A decreases with falling temperature, for $300 < T < 320$ MWM give the thermal conductivity as a constant (0.934 W cm^{-1} deg^{-1}) to within stated error limits of ±1%. Over the latter temperature range our chromium also would have had an apparently constant thermal conductivity (at about 1.025 W cm^{-1} deg^{-1}) if the random scatter had exceeded ±0.6%. However, our precision was such as to keep random scatter to better than ±0.2%. LM examined MWM's sample A only after it had been further annealed, and, although not providing a graph, reported for these temperatures a constant conductivity of 0.9365 W cm^{-1} deg^{-1} ± 0.17% in using $\Delta T = 0.5$ K (for a ΔT of 0.25 K, LM gave 0.9345 W cm^{-1} deg^{-1} ± 0.35%).

It is now pertinent and instructive to examine the effects of molybdenum impurities on the scattering processes in chromium. Arajs[2] has demonstrated that such additions strengthen the conduction-electron scattering below T_N and simultaneously lower T_N. Our measurements of the temperature dependence of the electrical resistivity on his Cr:Mo samples, which he has kindly lent to us, confirm his results exactly. Electrical resistivity data for two of these alloys, containing 0.6 and 5.1 at.% Mo, are provided in Figs. 2 and 3. We find moreover that the major features of the electrical-resistivity curves are present in the corresponding thermal-resistivity ones. These latter curves, along with the derived Lorenz functions, are also given in Figs. 2 and 3. The addition of 0.6 at.% Mo lowers the Néel point of chromium by about 7 K. Just as for the electrical resistivity, the effect on the thermal resistivity is conspicuous and it leads to a thermal-conductivity anomaly which maximizes at 305 K. But the clearest demonstration of all that, for this alloy system, the thermal-conductivity anomaly is magnified as the electrical-resistivity anomaly increases is provided by the 5.1-at.% alloy for which ρ_{min} locates at 244 K and λ_{max} (or W_{min}) at 247 K (Fig. 3). The thermal conductivity has a value at 247 K which is about 3.5% higher than if the alloy had on cooling remained paramagnetic. Furthermore the strong curvature of $\lambda(T)$ above λ_{max} [or of $W(T)$ above W_{min}] serves to show that fluctuations are effective in modifying the thermal conductivity at least as far as 255 K. It is clearly seen that for both of the alloys ρ_{min} is rounded off. This is likely to arise from short-range ordering effects at temperatures higher than the Néel point. By the reasoning given in our earlier paper,[1] the Néel point is more likely to be given by the location of $(d\rho/dT)_{\text{min}}$ than by ρ_{min}. In high-purity chromium this rounding is not always apparent. Sometimes the electrical resistivity near T_N seems to be almost discontinuous instead, resulting in a very sharp minimum. This may be the consequence of a first-order phase change, in which case there is little, if any, distinction to be made between the temperatures for ρ_{min} and for $(d\rho/dT)_{\text{min}}$.

Lastly, there is the interesting feature of the progressive enhancement of the Lorenz number in the magnetic phase-transition region caused by the molybdenum impurity additions. In the annealed pure chromium sample only a weak enhancement in the form of a shoulder near T_N is found (Fig. 1), but the addition of 5.1 at.% Mo (Fig. 3) generates a strong $2\frac{1}{2}\%$ anomalous peak in $L(T)$. This is mainly because of the effects in inelastic scattering, so that the thermal- and electrical-resistivity anomalies, besides being of different magnitudes, occur at different temperatures. For this reason the Lorenz function will always be expected to behave nonuniformly at magnetic transitions. It is also to be noted, in comparing the alloy re-

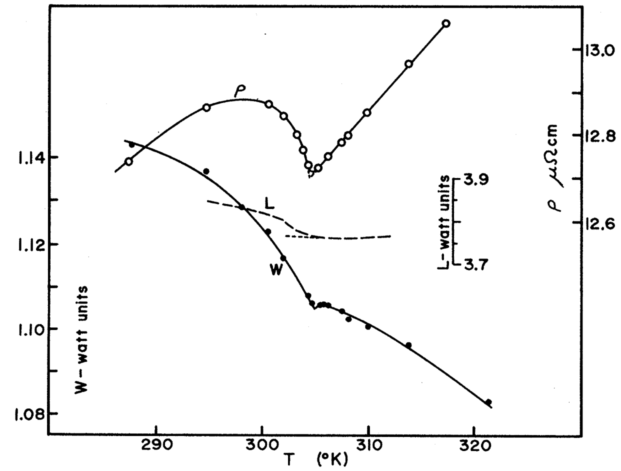

FIG. 2. Effect of the Néel transition on the thermal and electrical resistivities of a chromium alloy containing 0.6 at.% Mo. The Lorenz function in the region of T_N is also indicated.

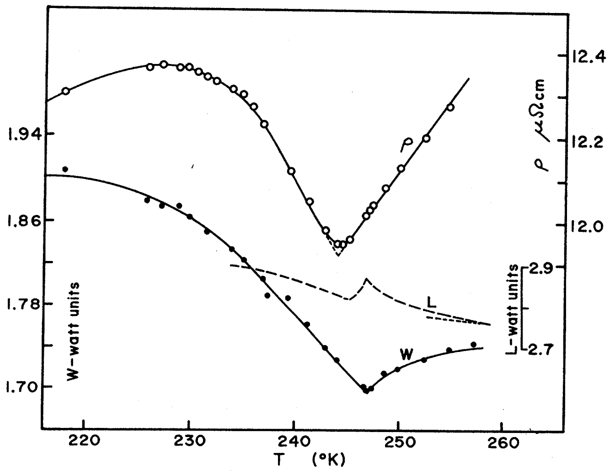

FIG. 3. Effect of the Néel transition on the thermal and electrical resistivities of a chromium alloy containing 5.1 at.% Mo. The Lorenz function in the region of T_N is also indicated.

sults (Fig. 2 and 3) with the pure chromium data (Fig. 1), that the electrical resistivity in the paramagnetic region rises as molybdenum is added while the thermal resistivity falls. This takes place in such a way that the magnitude of L falls quite rapidly. This unusual behavior, which also occurs in the antiferromagnetic region, can be completely understood in terms of energy-dependent band-structure effects which modify the basic electronic thermal conductivity of chromium and its alloys, and it will be explained in full elsewhere.

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LATTICE MODE DEGENERACY IN $\mathrm{MoS_2}$ AND OTHER LAYER COMPOUNDS

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The observed degeneracy of mutually exclusive infrared- and Raman-active modes in $\mathrm{MoS_2}$ is traced by means of group theory to the weak van der Waals interaction between layers.

We have recently carried out an experimental investigation[1] of the long-wavelength optical phonons in the hexagonal layer compound[2] $\mathrm{MoS_2}$ (molybdenite). The infrared-active mode for $E \perp c$ has been observed to be degenerate with one of the Raman-active modes in the basal plane. Since $\mathrm{MoS_2}$ possesses a center of inversion, the infrared- and Raman-active modes must be mutually exclusive. This is the first time that mutually exclusive modes in a layer compound have been observed to be degenerate. We shall show in this Letter that the observed degeneracy is not accidental, but is traceable by means of group theory to the weak van der Waals interaction between the layers. In addition, we predict that three optically inactive phonons will be degenerate with three optically active phonons. We further predict that mode degeneracy will prove to be characteristic of all layer compounds with more than one layer in the primitive unit cell.

Hexagonal $\mathrm{MoS_2}$, which belongs[3] to the space group D_{6h} ($P6_3/mmc$),[4] contains two molecular units and therefore six atoms within the primitive unit cell. Molybdenum and sulfur atoms are arranged in sheets parallel to the base of the hexagonal unit cell. One layer in the structure is composed of single sheets of sulfur atoms on both sides of a molybdenum sheet. For the $2H$ polytype of $\mathrm{MoS_2}$, the repeat distance along the c axis includes two of these layers. The short-range forces between atoms within a layer are