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Thermal Conductivity of Cr-Rich Cr-Si Between 3 and 300 K

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Abstract

The Cr-Si system exhibits above about 1 at% Si a large first order antiferromagnetic transition which is not well understood so far. Simultaneous measurements of thermal conductivity λ and electrical resistivity ρ on two Cr-Si alloys of 0.9 and 1.4 at% Si in the temperature range 3-300 K have been carried out to gain further insight into the role of electronic and lattice properties at the magnetic transition at the Néel point T_N . At T_N a step-like change in λ was observed for the Cr-1.4 at% Si alloy while λ was almost featureless for the lower concentration. The Lorenz number L, which was found to lie in the range 4-7 W Ω deg⁻², exhibits a broad peak centered around 60 K. Analysis of the λ -data reveals below 50 K a dominating lattice thermal conductivity term with a T^2 dependence and decreasing in magnitude with increasing Si concentration. Around T_N electronic contributions are found to dominate the thermal conductivity although both lattice and electronic effects seem to be responsible for the enhancement of L over the Sommerfeld value L_0 .

1. Introduction

Below the Néel temperature T_N (311K) Cr is an itinerant antiferromagnet with a transversely polarized incommensurate (I) spin-density-wave (SDW) structure. The magnetic transition at $T_{\rm N}$ shows a weak first order character. The stability of the ISDW is usually explained in terms of nesting between electron and hole octahedrons on the Fermi surface. Due to a slightly smaller size of the electron octahedrons compared to the hole ones this nesting is imperfect. Increasing the electron-to-atom ratio by alloying will expand the size of the electron surface eventually bringing about a perfect nesting thereby stabilizing a commensurate (C) SDW structure characterized by an increase of T_N with increasing solute concentration and a second order phase transition at T_N . However, there are striking exceptions to this "thumb-rule". Additions of Si to Cr not only decreases T_N to temperatures below 311K, but in addition gives a large first order paramagnetic (P)-CSDW transition at T_N with latent heats up to 5 times as large as that observed for the first order P-ISDW transition in pure Cr [1]. The first order character of the P-CSDW transition manifests itself also in other physical properties as the electrical resistivity ρ [2]. It is not clear why this first order transition occurs in Cr-Si. Recently Nakanishi and Kasuya [3] proposed a mechanism for the similar first order P-CSDW transition in Cr-Fe relating it to the interplay between the electron reservoir and a magnetoelastic energy term. It is possible that a similar explanation will hold also for the Cr-Si case. However, to have yet another approach to the understanding of the electronic and lattice properties of this system at the magnetic transitions we decided to make careful thermal conductivity studies on some Cr-Si alloys.

Thermal conductivity studies on Cr and Cr-alloys have been

rather scarce. Mostly the investigations on pure Cr have been centered on the understanding of the variation of the thermal conductivity coefficient λ around T_N from a critical phenomenon point of view or on the temperature dependence of the Lorenz number $L (= \lambda \rho / T)$ which is found to be considerably larger than its free electron value L_0 (2.45 × 10⁻⁸ WΩ deg⁻²) over a large temperature range (100-1300 K). The only dilute Cr-alloy systems studied to some extent so far are Cr-Mo [4,5] and Cr-V [5]. Mitchell and Goff [5] measured the thermal conductivity of Cr-Mo with 3.89 and 9.35 at% Mo and of Cr-V with 4.57 at% V between 3 and 300 K. The Cr-Mo alloys have an ISDW structure below T_N while the Cr-V alloy is paramagnetic in the whole temperature range studied. The lattice thermal conductivity λ_g derived from these data shows a maximum around 40–60 K. Below this maximum λ_g varies approximately as T^2 . The magnitude of λ_g obtained at these temperatures was however less than what could be expected theoretically. Point defect scattering from the Mo atoms could not explain these low values. It was found that λ_{e} increased with increasing Mo concentration in contrast to what could be expected from impurity scattering. Another significant feature of the results in [5] is the observed anomalously large L values with a complicated temperature dependence. For metallic conductors such large values, $3-4 \times 10^{-8}$ W-units, are usually explained in terms of increasing lattice contribution to λ . However, for both Cr and its alloys λ_g is too small to explain the observed increase in L for temperatures around T_N .

We present in this investigation simultaneous thermal conductivity and electrical resistivity studies on Cr-Si alloys of nominal compositions 0.9 and 1.4 at% Si. These concentrations were chosen because they lie on both sides of the tricritical point of the magnetic phase diagram of Cr-Si [1], the 0.9 at% alloy with the ISDW and the 1.4 at% alloy with the CSDW structure in the temperature region immediately below T_N . A short account of the results for Cr-1.4 at% Si has been presented previously [6].

2. Experimental details

The alloys investigated were from the same stock as used in previous latent heat and magnetic susceptibility [1], electrical resistivity [2] and neutron diffraction [7] studies on Cr-Si. The samples were in the shape of rods of ~35 mm length and a cross-section of $2 \times 2 \text{ mm}^2$. After preparation each of the samples were annealed at 1300 K for about 20 h to release possible strains and also improve the metallurgical homogeneity. λ was determined using a steady state longitudinal heat flow method in a standard He⁴ cryostat. In order to determine the temperature and the steady temperature gradient along the specimen a miniature thermometer bridge set-up has been developed. The bridge has a differential stability of $\pm \times 10^{-3}$ K

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Fig. 1. The electrical resistivity ρ for Cr-0.9 at% Si (\circ) and Cr-1.4 at% Si (Δ).



Fig. 2. The thermal conductivity λ for Cr-0.9 at% Si (\circ) and Cr-1.4 at% Si (\triangle). The inset shows λ at low temperatures and the lattice thermal conductivity λ_{g} estimated from eq. (2) for Cr-0.9 at% Si (\circ , •) and Cr-1.4 at% Si (\triangle , •).

over a long period. Further details of this technique will be published elsewhere. The error estimated for the measured λ depends on the temperature range. It is normally below 1% but increases somewhat for T < 20 K. ρ was determined with a four probe technique to within an accuracy of 10 ppm. ρ and λ were measured for increasing temperatures between 3 and 300 K.

3. Results and discussion

The ρ and λ data for the two Cr-Si alloys are plotted vs T in Figs. 1 and 2. While the resistivity anomaly around T_N for Cr-0.9 at% Si is similar to that observed for pure Cr with a P-ISDW transition, the first order P-CSDW transition in the Cr-1.4 at% Si alloy gives rise to a step-like change in ρ . These results agree with those reported earlier [2]. The additional anomaly observed for the 1.4 at% alloy at about 100 K was also seen in [2]. However it is only recently [8] on the basis of thermal expansion and subsequent phase diagram studies that this latter anomaly was attributed to a possible CSDW-ISDW transition. For both alloys the ρ vs T curves display shallow minima around 30 K, a phenomenon which has been observed also in other dilute Cr alloys.

The thermal conductivity λ is composed of lattice λ_g and electronic λ_e contributions. In an attempt to separate λ_g from λ_e we estimate the latter using the additive thermal resistivity approximation

$$1/\lambda_{\rm e} = W_{\rm e} = W_{\rm e0} + W_{\rm ei} + \Delta W \tag{1}$$

where W_e is the electronic part of the thermal resistivity, W_{e0} the thermal resistivity due to impurity scattering, W_{ei} the electron-phonon thermal resistivity and ΔW the thermal analogue of the deviations from the Matthiessen rule in the electrical resistivity case. At low temperatures the calculation of λ_e is facilitated by the fact that impurity scattering is dominating below about 50 K. W_e can therefore be approximated by $W_e \approx$ $W_{e0} = \rho_0/L_0 T$ (ρ_0 being the residual resistivity) assuming the validity of Wiedemann-Franz' relation. Deviations due to ΔW are assumed to be negligible at these temperatures. λ_g can then be estimated from

$$\lambda_{\rm g} = \lambda - L_0 T / \rho_0 \tag{2}$$

 λ_{g} as obtained from eq. (2) has been plotted for $T < 50 \,\mathrm{K}$ in Fig. 2 (see inset). The temperature dependence of λ_{g} is for both alloys close to a T^{2} -dependence as can be expected for a phonon dominated thermal conductivity scattering process at these temperatures. The alloy with the highest impurity concentration gives the lowest λ_{g} which is also what one should expect. In contrast to this Mitchell and Goff [5] found the inverse concentration dependence of λ_{g} from their measurements on Cr-Mo. The reason why Mo in Cr should give rise to such anomalous conditions is uncertain.

Eq. (2) cannot be used for calculation of λ_g above about 50 K due to the increasing inaccuracy in the estimation of λ_e from L_0 . If one assumes that the temperature dependence of λ_g is of the form A/T, where A contains contributions from both impurity and Umklapp scattering, and that λ_e is related to ρ through the Lorenz function L(T), λ can be described by

$$\lambda = L_{\rm e} T / \rho + A / T \tag{3}$$

where L_e is the value of L(T) obtained by fitting eq. (3) to the experimental data. Moore et al. [9] applied this relation to data

Table I.			
		$L_{\rm e} (10^{-8} {\rm W}\Omega {\rm K}^{-2})$	A (W m ⁻¹)
Cr-0.9 at% Si:	$T < T_{\rm N}$ $T > T_{\rm N}$	3.42 3.60	2680 1700
Cr-1.4 at% Si:	$\begin{array}{l} T < T_{\mathbf{N}} \\ T > T_{\mathbf{N}} \end{array}$	3.25 3.51	2460 1250

on pure Cr and found a good fit between 200 and 1300 K. For the Cr-Si alloys eq. (3) describes the experimental data well in a region from 160 K to well through T_N but with different values of $L_{\rm e}$ and A below and above $T_{\rm N}$. The values of $L_{\rm e}$ and A obtained from least-squares fit of eq. (3) to the experimental points are collected in Table I. The estimated error in the A and L_{e} -values is a few tenths of a percent. From these data it is obvious that the transition at T_N has rather little effect on λ_e while the changes in λ_g are more marked. The ratio λ_e/λ_g below $T_{\rm N}$ (referred to 230 K) is 3.3 for the 0.9 at% alloy and 2.6 for the 1.4 at% Si alloy. For $T>T_N$, λ_e/λ_g (at 250 K) is about 7 in both alloys. This should be compared with the λ_e/λ_g ratio for temperatures below 50K which is less than 1. These results demonstrate the dominance of λ_e around T_N while at low temperatures the importance of λ_g increases. The change in the $\lambda_{\rm e}/\lambda_{\rm g}$ ratio at $T_{\rm N}$ is mainly due to an increase of $\lambda_{\rm g}$ in the antiferromagnetic state compared to that in the paramagnetic state, λ_g being somewhat larger in relation to λ_e in the CSDW state (the 1.4 at% alloy) than in the ISDW state (the 0.9 at% alloy). This increase in magnitude of the lattice effects below T_N must be of magnetic origin. The values in Table I also reveal a decrease of λ_{g} , both below and above T_{N} , with increasing Si concentration, consistent with the results from the low temperature region.

In the antiferromagnetic state λ_e for the 1.4 at% alloy is somewhat smaller than λ_e for the 0.9 at% alloy. One possible reason for this is a decrease of the effective number of conduction electrons n_{eff} due to the energy gap which opens up over part of the Fermi surface below T_N . It is known that the energy gap for the CSDW state is larger than that for the ISDW state in Cr alloys [10]. This will cause a larger decrease of n_{eff} in the 1.4 at% alloy and hence explain the smaller λ_e in this alloy compared to λ_e for the lower concentration.

Compared to the rapid variation of ρ at T_N for the 0.9 at% alloy caused by the occurrence of the energy gap at the Fermi surface, λ for the same alloy is only weakly changing around the transition point. This is consistent with the result that λ is dominated by λ_e at these temperatures and the fact that λ_e is less sensitive to changes at the Fermi surface than ρ . For the 1.4 at% alloy the first order transition at T_N gives rise to a steplike change in λ similar to that observed in ρ . The reason for the occurrence of this first order transition in Cr-Si is not well understood but it may be related partly to magnetoelastic effects as suggested for the explanation of the similar P-CSDW transition in Cr-Fe [3]. The observed decrease of the λ_e/λ_g ratio below T_N for the 1.4 at% alloy compared to that in the $0.9\,at\%$ alloy could then be looked upon as a consequence of both a decrease of λ_{e} due to the larger energy gap and an increase of λ_e due to the increasing importance of the magnetoelastic effects in the 1.4 at% alloy.

 $T_{\rm N}$, determined from the resistivity derivative $(d\rho/dT)_{\rm min}$, is 236 K for Cr-0.9 at% Si and 238 K for Cr-1.4 at% Si. These



Fig. 3. Lorenz ratio L for Cr-0.9 at% Si (\circ), Cr-1.4 at% Si (\diamond) and pure Cr (---. From [11], sample Cr 2).

values agree within the limits of accuracy with the T_N values obtained in our latent heat and susceptibility measurements for corresponding concentrations [1]. When however applying a similar criterion, $(d\lambda/dT)_{max}$, to the thermal conductivity data it leads to a somewhat higher temperature, corresponding to an apparent shift of T_N of a few degrees. This is most easily seen for the 1.4 at% alloy with steps in both ρ and λ . In this case the shift is about 5 K. The reason for this different response of the electrical resistivity and the thermal conductivity to the transition may be a somewhat different influence of the critical fluctuations on the conduction electrons and on the phonon system and the fact that phonons seem to play a more important role for the changes in the thermal conductivity than for the changes in the electrical resistivity at the transition.

The Lorenz number calculated from the ρ and λ data for the Cr-Si alloys is much larger than L_0 . Furthermore it exhibits a broad maximum at about 60 K with a relatively smooth decrease towards higher temperatures, Fig. 3. For comparison L for pure Cr [11] is also shown in the same diagram. The drastic increase of L at low temperatures in the Cr-Si alloys compared to L for Cr is remarkable. A maximum in L at about the same temperatures as for Cr-Si was also observed for Cr-Mo and Cr-V [5] although L is even larger for Cr-Si than for the other Cr-alloys. This maximum is due to lattice effects.

Although the temperature dependence of L for temperatures below 200 K is quite different for the Cr-Si alloys compared to that for pure Cr, the L values above 230 K, i.e., around T_N , almost coincides indicating a possible common origin for the enhancement of L at these temperatures. It can moreover be noted that L_{e} obtained from fitting of eq. (3) in the temperature range around T_N is lower than L calculated from Wiedemann-Franz' relation. As the phonon contribution to λ has been subtracted in eq. (3) through the A/T-term, L_e contains only the electronic contribution to λ . Accordingly the $(L_e - L_0)$ -part of the enhancement should be due to electronic effects, probably band structure effects, while the $(L-L_e)$ part is probably connected with the contribution of λ_{g} to the Lorenz number. Hence both phononic and electronic effects seem to be responsible for the enhancement of L above L_0 around T_N . The fact that the transition at T_N is controlled both by electronic and lattice effects is consistent with the current theoretical picture [3] of the magnetic transitions in Cr-systems.

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