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Deviations from Matthiessen's rule for dilute Cu(Al) alloys

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Abstract. The electrical resistivity of a series of dilute polycrystalline Cu(Al) alloys has been investigated in the temperature range 4.2–300 K. The phonon part of the resistivity at low temperature varies as T^n where $4 < n < 5$. The temperature T_H corresponding to the maxima of the deviations from Matthiessen's rule $\Delta(c, T)$ obeys the Kagan–Zhernov law, i.e. $T_H \sim c^{1/5}$. At high temperatures the slope of $\Delta(c, T)$ depends on the impurity concentration and changes sign from negative to positive.

1. Introduction

In the past three decades, a great deal of experimental data have established the existence of large deviations from Matthiessen's rule (DMRs) for the electrical resistivity of polyvalent and noble metals containing non-magnetic impurities [1, 2]. In parallel with the experimental activities considerable theoretical attempts have been reported in order to explain the observed DMRs. Bass [1] and Wiser [3] have described and critically reviewed various theoretical approaches to account for the DMR. The experimental data show that the most salient features of the DMR of polyvalent and noble metals are (i) a monotonic increase at low temperatures, which does not follow a simple power law with temperature, (ii) a maximum, called a 'hump', at intermediate temperatures, which becomes more and more pronounced with decreasing concentration of alloying atoms and (iii) the fact that at high temperatures DMR either varies linearly with temperature with positive or negative slope or is temperature independent.

As a physical reason for the large observed DMR Bass [1], in his comprehensive review article, proposed a total of 14 different explanations. In the early 1980s Kaveh and Wiser [4, 5], in two important papers, developed a theoretical framework in which they attempted to provide a natural explanation for the magnitude of the DMRs of polyvalent and noble metals, their temperature dependence, their approximate $\log(\rho_0)$ dependence of $\Delta\rho$, and their 'humps'. Their approach is based on the fact that, at low temperatures, the electron–phonon scattering probability for these metals is very anisotropic over the Fermi surface. The electrons, occupying a relatively small portion of the Fermi surface in the vicinity of the Brillouin zone boundaries, are scattered much more strongly than those on the rest of the Fermi surface. Analysing the phenomena associated with the large DMR, Kaveh and Wiser have used the variational formulation of the Boltzmann equation, based on a new deviation electron distribution function, which incorporates explicitly the extremely large anisotropy over the Fermi surface of the electron–phonon scattering probability. Using this procedure Kaveh and Wiser obtained excellent agreement with the resistivity data of dilute aluminium alloys both as a function of temperature and as a function of impurity concentration.

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The linear dependence of $\Delta(c,T)$ on temperature at high temperatures has been attributed by Kagan and Zhernov [6, 7] to interference between scattering of electrons from phonons and from impurities. According to their detailed calculation, the sign of the slope of the linear part of $\Delta(c,T)$, i.e. $\rho_0^{-1}\,\partial\Delta(c,T)/\partial T$, would usually be the same as the sign of the difference between the ionic charges of the impurity and the host ion in the lattice. An alternative derivation by Bhatia and Gupta [8] yielded similar results. According to their model the interference term should lead to a linear dependence of the relative DMR $\Delta(c,T)/\rho_0$ on T and the sign of the slope is determined by the sign of an integral whose argument contains the difference between the form factors for the impurity and the host ion.

Previous investigations of the DMR on Al(Cu) dilute alloys [9] have indeed displayed the above-mentioned features. Especially in the high-temperature region, $\Delta(c,T)/\rho_0$ is linear in T with a weak negative slope. This result is in agreement with the Kagan–Zhernov [6, 7] calculation because the difference of the valence between Cu impurity and Al host is negative.

The purpose of the present investigation is to study the influence of Al impurities on the Cu DMR and in particular to examine the validity of the theory by Kagan and Zhernov [6, 7] and Bhatia and Gupta [8].

2. Experimental procedure

The electrical measurements were performed on polycrystalline samples, of pure copper (99.999%, supplied by ASARCO) with residual resistivity ratio of 1600 and copper alloyed with 60, 140, 270, 560, 1000, 2500 and 5000 ppm aluminium (99.999% supplied from VAM, Bonn, Germany). The alloys were prepared by HF levitation melting and then rolled into foils of about 100 μm thickness. The Al concentration was determined by chemical analysis with an accuracy of ± 0.006 wt%. The specimens of the alloys were annealed for 24 h at 900 °C in a vacuum ($<10^{-5}$ mbar), while the pure copper samples were annealed under a low pressure of oxygen to remove the effects of magnetic impurities. The Cu(Al) alloys were in the solid solution region, as evidenced by the residual resistivity, which was always proportional to the impurity concentration. The residual resistivity per atomic per cent was $\Delta\rho/c = 1.14\ \mu\Omega$/at.%, which is in very good agreement with previous measurements [10, 11]. The experimental setup for the measurements of the electrical resistance has been described previously [12]. The main errors in the values of the restivities can be attributed to the inaccuracy in the determination of the geometrical factor ($\pm 0.5\%$).

3. Results

The relative DMRs, $\Delta(c,T)/\rho_0$, for seven Cu(Al) alloys are plotted as a function of temperature T in figure 1. The DMR $\Delta(c,T)$ is defined by the relation

$$\Delta(c,T) = \big[\rho_a(T) - \rho_p(T)\big] - \big[\rho_a(4.2\ \mathrm{K}) - \rho_p(4.2\ \mathrm{K})\big] \tag{1}$$

where $\rho_a(T)$ and $\rho_p(T)$ are the phonon-induced resistivities for the alloyed and pure samples, respectively. The relative DMRs show the following features: at low temperatures $\Delta(c,T)/\rho_0$ increases with temperature, while at intermediate temperatures the DMRs show maxima that become more and more pronounced with decreasing concentration and which shift with concentration. In the high-temperature region, $\Delta(c,T)/\rho_0$ are linear in T, but the sign of the slope changes from negative to positive as the aluminium concentration increases. For the alloy with 1000 ppm Al the slope $\Delta(c,T)/T$ is zero. Similar behaviour in the high-temperature region has been found by Panova *et al* [13] in the DMR of Mg(Pb)

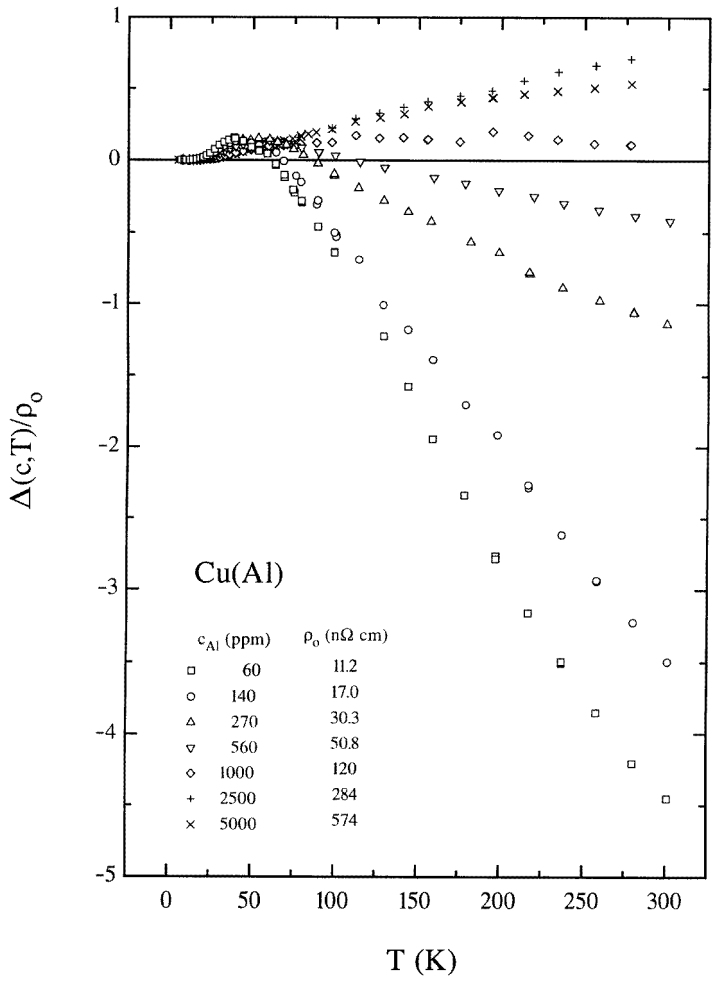

Figure 1. Relative DMR $\Delta(c, T)/\rho_0$ as a function of temperature for Cu(Al) alloys.

alloys, but the change of the slope goes from negative to positive as the Pb concentration increases.

Figure 2 shows the quantity $[\rho_a(T) - \rho_0]/T^4$, instead of the relative DMR $\Delta(c, T)/\rho_0$, as a function of T in a double-logarithmic plot. $\rho_a(T)$ is the measured resistivity of the alloys at the temperature T. $\rho_a(T) - \rho_0$ of the pure copper and the alloy with 60 ppm aluminium varies aproximately as T^4 in the temperature range 6–12 K. As the temperature increases up to 35 K, $\rho_a(T) - \rho_0$ goes over to T^5 dependence. The alloys with aluminium concentration greater than 60 ppm show only a T^5 dependence for temperatures above 10 K. For temperatures lower than 10 K the resolution of the measurements was insufficient and so it was impossible to observe any temperature dependence.

Figure 3 shows the dependence of the phonon resistivity $\rho_a(T) - \rho_0$ on the residual resistivity, ρ_0, in a semilogarithmic plot for a series of fixed temperatures. These temperatures are chosen in order to be nearly the same as those in the review article by Cimberle *et al* [2]. The dashed straight lines which are drawn through the experimental data at fixed temperatures show that the phonon resistivity $\rho(T) - \rho_0$ below a certain definable

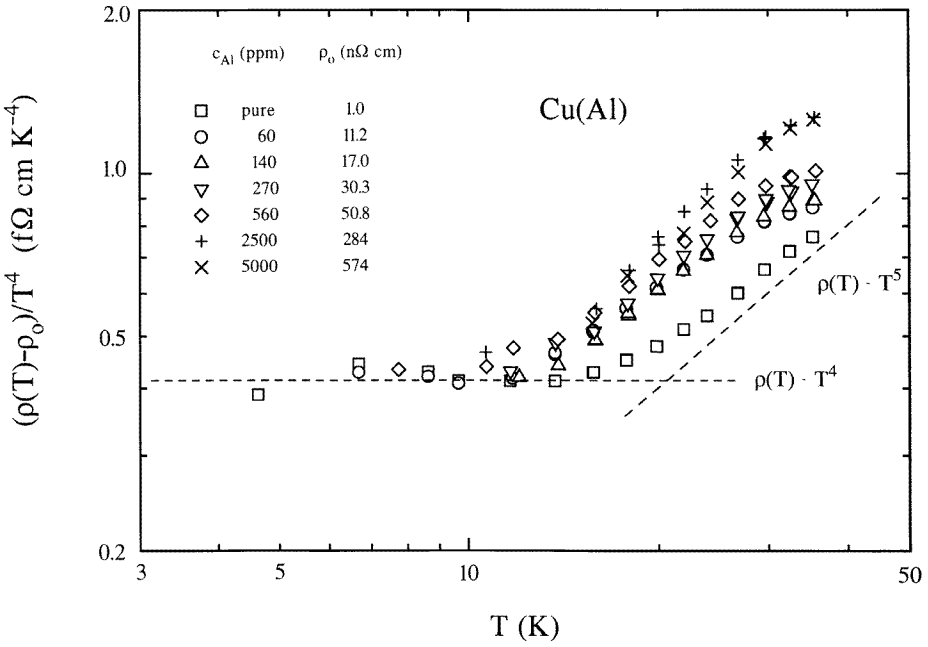

Figure 2. Temperature dependence of $[\rho(T) - \rho_0]/T^4$ for Cu(Al) alloys.

value of the residual resistivity ρ_0 is constant, which means that Matthiessen's rule is valid, while above this value $\rho(T) - \rho_0$ depends logarithmically on ρ_0, i.e. Matthiessen's rule is not valid. The full curve at 15.7 K represents the calculated values of the phonon resistivity $\rho(T) - \rho_0$ as a function of ρ_0 [14]. This graph shows that there is no indication for a saturation of $\rho(T) - \rho_0$ for samples having higher values of ρ_0 as predicted by the theoretical calculation.

4. Discussion

The excitation of thermal vibrations in the perturbed lattice, which in general differ from those in the ideal lattice, can give rise to a temperature dependence of the defect-induced resistivity. A large number of calculations of the phonon resistivity $\rho(T)$ for noble metals in the 'dirty' limit have been based on two-plane-wave pseudo-wavefunctions and a realistic Fermi surface.

Recently Bergmann *et al* [14] calculated the low-temperature resistivity $\rho(T)$ of noble metals using a variational solution of Boltzmann's equation. In order to calculate the electron–phonon scattering matrix elements, they used an anisotropic Fermi surface, multi-plane-wave pseudo-wavefunctions and an electron distribution function which contains both angular and energy dependence.

Based on these assumptions, Bergmann *et al* [14] calculated the temperature dependence of the electron–phonon scattering term $\rho_{ep}(T)$ for noble metals and they found the following features. (i) For $T < 3$ K, $\rho_{ep}(T) \sim T^5$; however, at these low temperatures, the electron–electron scattering term $\rho_{ee}(T)$ also makes an important contribution; the sum of these two contributions varies very closely with T^4. (ii) In the temperature region $T \sim 5$–6 K, a direct calculation of the electron–phonon part, $\rho_{ep}(T)$, shows that $\rho_{ep}(T)$ follows the power law

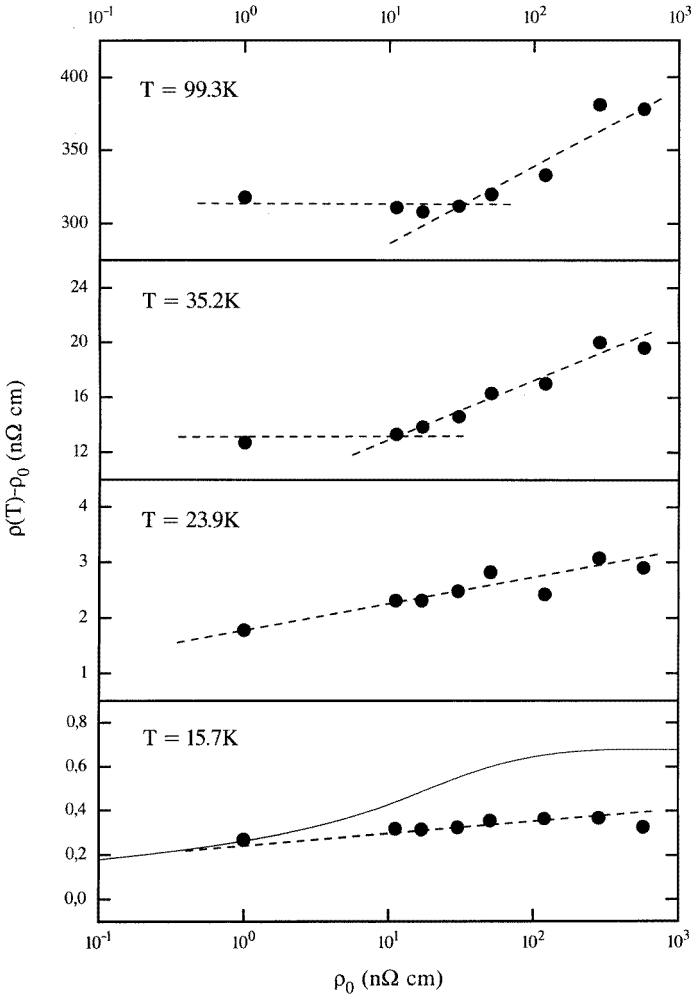

Figure 3. $\rho(T) - \rho_0$ as a function of the residual resistivity ρ_0 for different fixed temperatures. The full curve at 15.7 K is that calculated by Bergmann *et al* [14].

$T^{n(T)}$, where $n(T) \sim 4.0$–4.5, for values of residual resistivity ρ_0 in the nanoohm centimetre range. In this temperature region the contribution of $\rho_{ee}(T)$ to $\rho(T)$ is relatively small but large enough to reduce the apparent power law of $\rho(T)$ to about T^4.

A T^4 dependence of the resistivity was also found in Ag-based alloys in the temperature range 1.2–9 K by Barnard *et al* [15], which means that the two systems behave similarly.

The T^4 dependence of the resistivity in the present pure copper sample and the alloy with 60 ppm Al in the temperature range 4.2 K $< T <$ 10 K can be attributed to the contributions from both electron–phonon and electron–electron scattering as discussed by Bergmann *et al* [14].

As the temperature increases above 10 K the electron–electron scattering term becomes ineffective and the net effect is due only to electron–phonon scattering. By increasing the Al concentration, the T^4 dependence of the resistivity disappears and a T^5 dependence is observed in the temperature range 10 K $< T <$ 35 K. Similarly, a T^5 dependence has

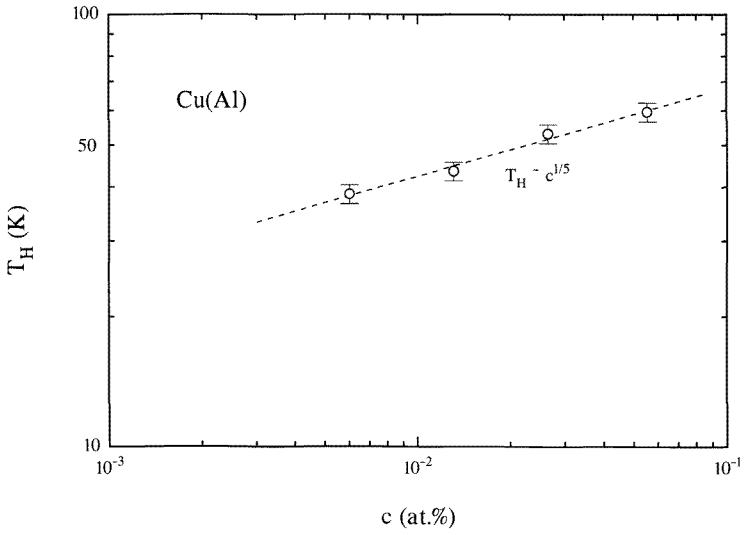

Figure 4. T_H against solute concentration c.

been found also in the temperature range 10 K $< T <$ 35 K by Lengeler *et al* [16] for Cu(Au) and Cu(Ni) alloys. These authors have explained their results using the Kagan–Zhernov [6] theory, where they have taken into account the inelastic coherent scattering. According to the Kagan–Zhernov calculation, if the atomic mass of the impurities is much larger than that of the host lattice atoms a resonance in the scattering of phonons at the impurities can occur. This is also the case for Au in Cu but not for Ni and Al. On the other hand, Brett and Black [17] calculated numerically the resistivity of copper at temperatures below 20 K using variational calculations. Their results indicate a T^5 behaviour with a magnitude of ρ/T^5 of about 0.035×10^{-9} $\mu\Omega$ cm K^{-5}. These results are in good agreement with the present measurements, which, as show in figure 2, give, at $T = 20$ K, for $[\rho(T) - \rho_0]/T^5$ values between 0.030 and 0.038×10^{-9} $\mu\Omega$ cm K^{-5} for the Cu(Al) alloys and 0.024×10^{-9} $\mu\Omega$ cm K^{-5} for the pure copper.

At intermediate temperatures the characteristic feature of the DMR is the appearence of the 'hump', which shifts with the Al concentration. Figure 4 shows the temperature T_H, corresponding to the 'hump' of $\Delta(c, T)$, as a function of the Al concentration in a log–log plot. This diagram shows that T_H varies proportionally with $c^{1/5}$, except for the Cu(Al) alloys with the largest impurity concentrations where T_H was not easy to determine due to washing out of the 'humps'. The phenomenon of the 'hump' has been studied very extensively for aluminium, with detailed data available for many different types of impurity [18–22].

The appearance of the 'hump' in the DMR and the shift of its position with concentration as $c^{1/5}$ was demonstrated by Kagan and Zhernov [6, 7]. They showed that the $T_H \sim c^{1/5}$ law can be attributed to the change in the anisotropy of the nonequilibrium electron distribution. This anisotropy is mainly caused by the Umklapp processes in electron–phonon interaction and is also a result of the anisotropy of the phonon spectrum, which also exists in a spherical Fermi surface. By adding impurities in a host metal the anisotropy of its nonequilibrium electron distribution function is smoothed out.

Under the assumptions that the metal is simple cubic, its Fermi surface is spherical and

its phonon spectrum consists of three branches of equal frequency with polarization along the crystal axes, Kagan and Zhernov [7] calculated the pure metal resistivity and found the expression

$$\rho_p(T) = \rho'_p(T)[1 - \eta(T)] \tag{2}$$

where $\rho'_p(T)$ is the ideal resistivity calculated using an isotropic electron distribution function, and $\eta(T)$ is a function which depends upon the existence of anisotropy. This anisotropic parameter $\eta(T)$ can be determined from the approximate relation

$$\eta(T_H) \sim \Delta(c, T_H)/\rho_0(c) \tag{3}$$

where $\Delta(c, T_H)/\rho_0(c)$ is the maximum experimental value of the DMRs, which occur at the 'hump' temperature T_H. Figure 5 shows $\Delta(c, T_H)/\rho_0(c)$ of the present samples as a function of T_H/Θ_D together with the values for other copper alloys [16, 23]. As Debye temperature the value $\Theta_D \sim 343$ K (of pure copper) [24] is used, under the assumption that at these impurity concentrations Θ_D remains unchanged. The dashed curve represents the anisotropy function $\eta(T)$ which was obtained by Kagan and Zhernov [7], for a simple cubic metal with a spherical Fermi surface and a phonon spectrum corresponding to the nearest-neighbour interaction. A comparison between the calculated $\eta(T)$ curve and the experimental $\Delta(c, T)/\rho_0$ values for different copper alloys shows that for the systems Cu(Al), Cu(Ge) [23] and Cu(Sn) [23] there is relatively good agreement, while for the systems Cu(Au) [16, 23] and Cu(Ni) [16] the $\Delta(c, T)/\rho_0$ data are about an order of magnitude larger than the calculated value $\eta(T)$. Figure 4 shows also that the temperature T_H corresponding to the 'hump' becomes strongly dependent on the concentration and shifts to higher temperatures as the concentration c increases, where the anisotropy parameter $\eta(T)$ decreases. This means that the nonlinear effects are weak in the dirty specimens. The cause of this nonlinear effect is the suppression of the anisotropy of the distribution function due to elastic scattering on the impurities. It must be mentioned here that an important conclusion to be drawn from the Kagan–Zhernov studies is that their calculation is an idealized model (spherical Fermi surface, one-OPW electron wave function, incorrect electron distribution function, etc) and so cannot yield quantitatively reliable results. On the other hand, as mentioned above, Kaveh and Wiser [4, 5], using a variational formulation of the Boltzmann equation, were the first to show quantitatively that the existence of the 'hump' and its shift with impurity concentration as $c^{1/5}$ for Al alloys can be related directly to the function $\Phi(\boldsymbol{k})$ which describes the variation of the electron distribution function $f(\boldsymbol{k})$ from the equilibrium value $f_0(\boldsymbol{k})$. A comparison of the characteristics of the 'humps' for the aluminium and copper alloys which are reported in the literature shows that if there are any differences they are not significant. This may mean that the same mechanism is responsible for the appearance of the 'hump' in both systems.

As regards the high-temperature region, as mentioned in section 1, the linear dependence of $\Delta(c, T)/\rho_0$ on the temperature T and the sign of the slope $\rho_0^{-1}\,\partial\Delta(c, T)/\partial T$ of the Cu(Al) system can be explained using either the Kagan–Zhernov [6, 7] or the Bhatia–Gupta model calculations [8].

According to the Kagan–Zhernov rule the slope of the Cu(Al) system at high temperatures must be positive in contrast to the Al(Cu) system, because the valence difference between aluminium impurity and host copper is positive. This prediction is in accordance with the results of our two most concentrated Cu(Al) alloys, while it is in disagreement with the results of the less concentrated alloys, which show negative slopes. The discrepancy in the sign of the slopes between the most and least concentrated alloys can be attributed to the presence of residual Fe impurities in the initial pure Cu from which

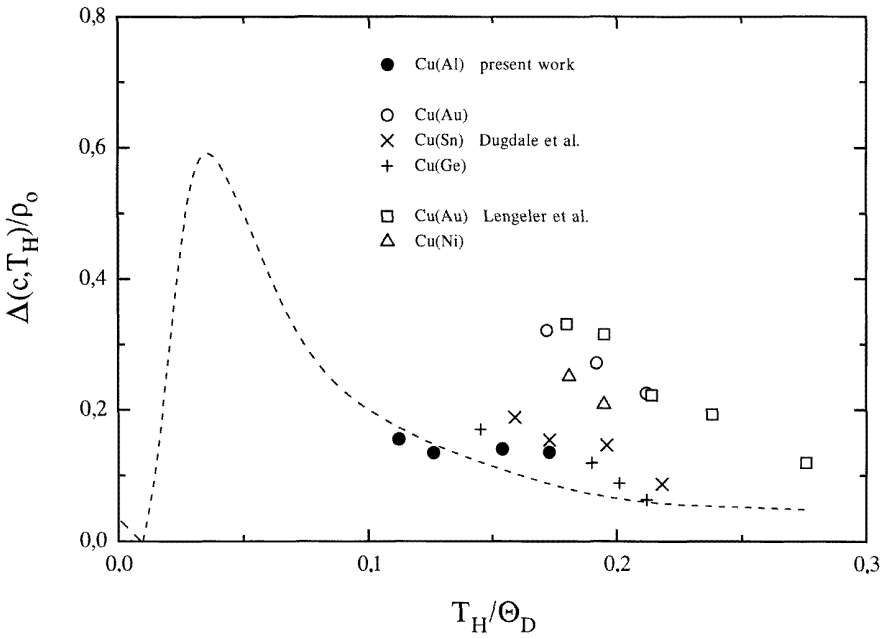

Figure 5. The maximum experimental values of DMR $\Delta(c, T_H)/\rho_0$ as a function of T_H/Θ_D together with the $\eta(T)$ function for different copper alloys.

the alloys are prepared. It is worth mentioning that previous investigations on Cu-based alloys containing Fe impurities [25] showed that the DMR has a negative slope at high temperatures. If we assume that the existing residual Fe impurities in the pure Cu used in the present work cause a DMR with negative slope at high temperatures, this slope will normally decrease as the concentration of added Al impurities increases, because the scattering of the electrons on Al will compensate for the scattering on the residual Fe impurities. In the most concentrated Cu(Al) alloys the prevailing scattering comes from Al impurities and so the DMR must have a positive slope according to the Kagan–Zhernov rule.

5. Conclusions

The measurements reported in this work show that the temperature dependent resistivity of pure copper and a Cu(Al) alloy with 60 ppm Al, below 12 K, varies as T^4, while in the temperature range 10 K $< T <$ 35 K it varies as T^5. Values for all other Cu(Al) alloys measured display T^5 dependence in the same temperature range. At intermediate temperatures, the relative DMR $\Delta(c, T)/\rho_0$ shows a hump, whose corresponding temperature T_H shifts with impurity concentration as $c^{1/5}$. This result agrees with the theory of Kagan and Zhernov. In the high-temperature region the relative deviation $\Delta(c, T)/\rho_0$ depends linearly on T and has a negative slope for the alloys with low concentration, while the high-concentration alloys show a positive DMR. The negative slope for the alloys with small Al concentration is attributed to the presence of Fe residual impurities.

Acknowledgments

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