PHYSICAL REVIEW B VOLUME 47, NUMBER 20 15 MAY 1993-II

Deviations from Mathiessen's rule for dilute Al-Li alloys

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(Received 28 September 1992)

The temperature-dependent part of the electrical resistivity of polycrystalline Al-Li dilute alloys in a wide range of conentration of Li has been measured from 4.2 to 300 K. The phonon resistivity of the alloys varies as T^n, where $2 \leq n \leq 5$. At intermediate temperatures the deviation from Mathiessen's rule (DMR) for the alloys with low-impurity content passes through a broad maximum and the corresponding temperature depends on the impurity concentration as $\sim c^{1/5}$. At high-enough temperatures the DMR $\Delta(c,T)/\rho_0$ changes sign from negative values to positive as the Li concentration increases.

I. INTRODUCTION

Since 1970, an enormous number of experimental data have established the existence of large deviations from Mathiessen's rule (DMR) for the low-temperature resistivity of polyvalent and noble metals.[1] Although large DMR are observed for all polyvalent metals, the DMR for aluminum has been measured more extensively than for any other metal, because of the experimental advantages of Al. Bass[2] has summarized the DMR in Ref. 2. At the same time a considerable number of theoretical calculations have been made in order to understand the observed DMR.[3,4]

In the course of time the investigations of the DMR have become a very important tool in order to understand the various scattering mechanisms of the conduction electrons in metals. There is a large number of possible scattering processes[1] that are responsible for the appearance of DMR.

Until now the temperature-dependent part of the electrical resistivity of dilute Al-Li alloys has not been investigated and only the isochronal annealing and aging processes of Al-Li alloys have been studied.[5] The purpose of the present investigation is to measure the phonon resistivity of the Al-Li dilute alloys (α-phase) in order to study the scattering processes.

II. EXPERIMENTAL PROCEDURE

The measurements were performed on polycrystalline specimens of about 100-μm thickness. The samples were pure aluminum (supplied from VAW, Bonn, FRG) with a residual resistivity ratio of 5.500 and aluminum alloyed with 0.011-, 0.022-, 0.044-, 0.104–0.191-, 0.371-, 0.541-, 1.20-, and 3.41-at. % Li. A master Al-Li alloy was first prepared by melting and casting 99.9999% Al and 99.9% Li in a glove box under argon atmosphere and using a crucible of boron nitride. The dilute alloys were produced from the master alloy in an induction furnace using a second BN crucible. The concentrations were determined by atomic absorption spectroscopy. The alloys were annealed at 450 °C in vacuum ($\sim 10^{-5}$ mbar) and were in solid solution state as evidenced by the residual resistivity measurements, which were proportional to the impurity concentration. The residual resistivity per atomic percent Li at 4.2 K was 33×10^{-8} Ω cm, while at 77 K was 71×10^{8} Ω cm.[6] In comparison to the present value at 77 K, Ceresara, Giarda, and Sanchez[5] have found a residual resistivity of 80×10^{-8} Ω cm/at. %. The discrepancy between these two values at 77 K can be either attributed to the determination of the Li concentration or to the geometry factor. The experimental arrangement for the electrical resistance measurements has been described previously.[7] The main errors in the values of the resistivity can be attributed to the inaccuracy in the determination of the geometry factor ($\pm 0.2\%$).

III. RESULTS

In Fig. 1 the relative deviations from Mathiessen's rule $\Delta(c,T)/\rho_0$ for several Al-Li alloys are plotted as a function of temperature. The departure from Mathiessen's rule is given by the expression

$$\Delta(c,T) = [\rho_a(T) - \rho_p(T)] - (\rho_a^0 - \rho_p^0) , \tag{1}$$

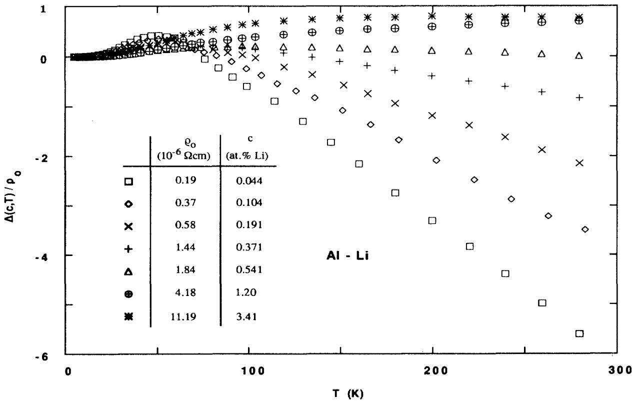

FIG. 1. Relative deviation from Mathiessen's rule as a function of temperature for Al-Li alloys.

where $\rho_a(T)$ and $\rho_p(T)$ are the phonon-induced resistivities, and ρ_a^0 and ρ_p^0 are the residual resistivities for the alloyed and pure samples, respectively. At low temperatures $\Delta(c,T)/\rho_0$ is positive and increases slowly with temperature. For temperatures above 40 K, $\Delta(c,T)/\rho_0$ shows a flat maximum which shifts with Li concentration, while in the high-temperature region $\Delta(c,T)/\rho_0$ depends on the impurity concentration. For the alloys with low Li content $\Delta(c,T)/\rho_0$ varies approximately linearly with temperature and is negative, while for the three alloys with sufficient large Li concentration the maxima are washed out and $\Delta(c,T)/\rho_0$ becomes nearly temperature independent and positive.

The low-temperature behavior of the temperature-dependent part of the electrical resistivities of pure Al and Al-Li alloys is presented in Fig. 2, where the quantity $[\rho(T)-\rho_0(4.2\text{ K})]/T^3$ is plotted as a function of temperature in a log-log plot. $\rho(T)$ is the measured resistivity at the temperature T. From this plot it can be seen that the phonon resistivity $\rho(T)-\rho_0$ of the pure Al and Al-Li alloys cannot be characterized by a simple power law. The figure shows that the phonon resistivity of pure Al and the first two Al-Li alloys with the lower concentration have nearly the same temperature dependence. Between 4.2 and 9 K the quantity $\rho(T)-\rho_0$ is proportional to T^3 for pure Al, while for the two alloys the quantity is proportional to $T^{2.5}$. As the temperature increases (9–18 K) $\rho(T)-\rho_0$ goes over to a $T^{2.5}$ dependence for the pure Al, while for the alloys $\rho(T)-\rho_0$ remains proportional to $T^{2.5}$. In the range 18–27 K the phonon resistivity both of pure Al and of the two alloys is proportional to T^3 and as the temperature increases (27–60 K) $\rho(T)-\rho_0$ varies as T^5. By increasing the Li concentration the T^5 law behavior $\rho(T)-\rho_0$ begins to disappear, while the temperature region, where the T^3 dependence is valid, becomes enlarged. For the two most concentrated Al-Li alloys the phonon resistivity $\rho(T)-\rho_0$ exhibits a T^2 dependence in the temperature range 5–15 K and a T^3 behavior between 15 and 50 K. Above about 120 K the variation of $\rho(T)-\rho_0$ is proportional to T for all alloys.

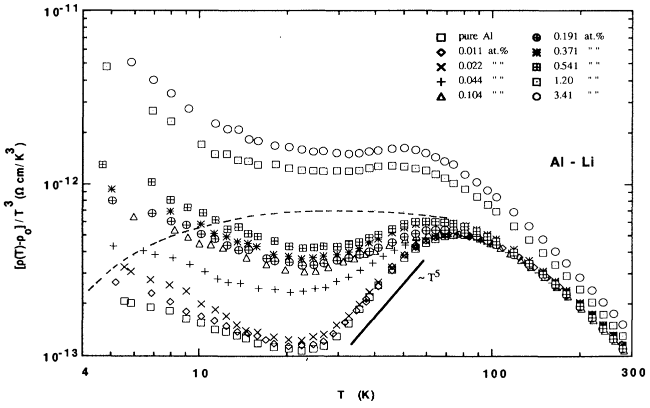

FIG. 2. Variation of $[\rho(T)-\rho_0]/T^3$ with temperature for Al-Li alloys.

IV. DISCUSSION

There is a large number of theoretical model calculations which attempt to interpret the low-temperature-dependent part of the resistivity of pure and dilute alloyed aluminum. Most of these calculations point out the importance of the electron-phonon umklapp scattering at low temperatures.[3,4,8] Lawrence and Wilkins[8] have calculated the phonon resistivity $\rho_{e\text{-ph}}$ of polyvalent metals (Al and Zn) in the "dirty limit" and they have found that below some characteristic temperature $\Theta_1(T<\Theta_1)$, which is of the order $0.01-0.05\Theta_D$ (Θ_D is the Debye temperature, for Al $\Theta_D=395$ K), umklapp processes contribute to the phonon resistivity as T^5. This T^5 behavior of the resistivity has a coefficient which is greater than that of Bloch resistivity ρ_{Bloch} due to phonon normal processes. On the other hand, for temperatures $T>\Theta_1$ the phonon resistivity $\rho_{e\text{-ph}}(T)$ due to umklapp processes cannot be characterized by a single power law of T. In this case $\rho_{e\text{-ph}}(T)$ increases more slowly than T^5 and is given by two leading terms with temperature dependence T^2 and T^4. In Fig. 2 the dashed curve represents the theoretical calculation of Lawrence and Wilkins. A comparison with the experimental data shows that the form of the calculated resistivity in the temperature range 20–80 K exhibits the same temperature dependence as the resistivity of the samples with the highest Li concentration but it is about a factor of 3 smaller.

Kaveh and Wiser[3,4] have calculated in detail the low-temperature resistivity of dilute aluminum alloys by the variational formulation of the Boltzmann equation, based on the special properties of the electron distribution function. This function incorporates explicitly the extremely large anisotropy over the Fermi surface of the electron-phonon scattering probability. Their results also do not yield a single power-law behavior for the temperature dependence of resistivity.

The characteristic feature of DMR at intermediate temperatures is, as mentioned above, the flat maximum, which shifts with the Li concentration. In Fig. 3 the temperature T_H corresponding to the broad maximum of $\Delta(c,T)$ is plotted as function of the Li concentration in a double logarithmic diagram. This plot shows that T_H ex-

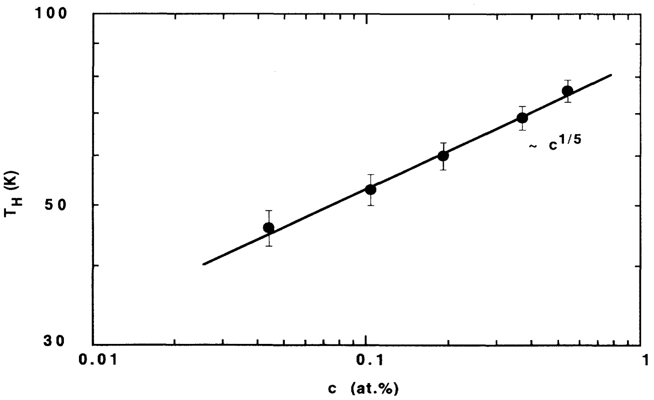

FIG. 3. T_H vs solute concentration c.

hibits the same behavior as other Al alloys,[7,9,10] i.e., T_H varies proportional to $c^{1/5}$, except for the three Al-Li alloys with the largest impurity content. For these three samples, T_H was not easy to determine, because of the washing out of the broad maximum.

The existence of the broad maximum in DMR and the shift of their position with concentration as $\sim c^{1/5}$ was stated by Kagan and Zhernov.[11,12] According to their calculation the $T_H \sim c^{1/5}$ law is attributed to the change in the anisotropy of the electron distribution function. This anisotropy mainly arises as a result of umklapp processes in electron-phonon interaction, and also as a result of anisotropy of the phonon spectrum and exists in the case of a spherical Fermi surface.

With these assumptions they have obtained for the resistivity of a pure metal the expression

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

where $\rho_p'(T)$ is the resistivity calculated using only the isotropic term and $\eta(T)$ is a function dependent on the anisotropy. In the presence of small amounts of impurities in the metal they found for the departure from Mathiessen's rule an expression which has the form

$$\Delta(c,T)=\Delta'(c,T)+\rho_p'(T)\eta(T)\left[1-\frac{1}{1+cR/P(T)}\right] . \tag{3}$$

$\Delta'(c,T)$ is calculated by the use of an isotropic distribution function and R and $P(T)$ are integrals arising from the elastic scattering of the electrons by the impurities and from electron-phonon scattering in the pure metal, respectively. At intermediate temperatures, where $P(T)\sim cR$ is valid, that is the case when the $\rho_p'(T)$ is comparable with the residual resistivity ρ_0, the magnitude of the impurity resistivity itself turns out to be large, namely

$$\Delta(c,T)/\rho_0(c)\sim\eta(T) . \tag{4}$$

Kagan and Zhernov[12] have shown that by a characteristic temperature $\tilde{T}$, where $P(T)=cT$, the calculation yields the law

$$\tilde{T}\sim c^{1/5} \tag{5}$$

because $P(T)\sim T^5$. $\tilde{T}$ is nearly equal to the temperature T_H corresponding to the maximum of the DMR. Figure 4 shows the experimental values of the deviation from Mathiessen's rule $\Delta(c,T_H)/\rho_0$, which occur at the temperature of maximum T_H, as a function of $\tilde{T}/\Theta_D$ together with other aluminum systems.[9,13–16] As Debye temperature Θ_D, the value $\Theta_D=428$ K of pure aluminum[17] is used for all alloys, because we expect that at these impurity concentrations Θ_D does not change drastically. Figure 4 shows also the temperature dependence of the anisotropy function $\eta(T)$ (dashed curve) obtained by Kagan and Zhernov.[12] In order to calculate the function $\eta(T)$ Kagan and Zhernov[12] have assumed a simple cubic lattice with a spherical Fermi surface and a phonon spectrum corresponding to the nearest-neighbor interaction. The phonon spectrum consists of three branches of equal frequency with polarization along the cubic axes. For polarization oscillations along the x axis they have taken the dispersion relation

$$\omega_q^2=\frac{k_B^2}{2.4\hbar^2}\Theta_D^2\{1-\xi\cos(q_x\alpha_x)-\tfrac{1}{2}(1-\xi)[\cos(q_y\alpha_y)+\cos(q_z\alpha_z)]\} , \tag{6}$$

where k_B is the Boltzmann's constant, α_x,α_y, and α_z are the lattice vectors, and ξ is the parameter characterizing the phonon spectrum anisotropy.

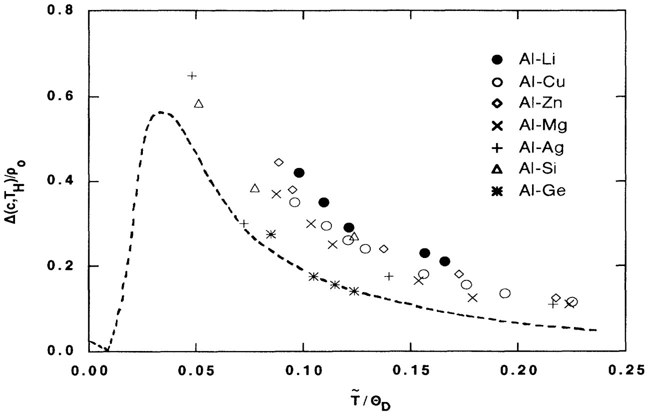

FIG. 4. The maximum experimental values of DMR $\Delta(c,T_H)/\rho_0$ as a function of $\tilde{T}/\Theta_D$ where $\tilde{T}$ is equal to T_H, the temperature of the broad maximum together with the $\eta(T)$ function calculated by Kagan and Zhernov.

For the transition probability $W(\mathbf{k},\mathbf{k}')$, they have used expressions calculated in the first Born approximation, using the scattering correlation function of van Hove,[11] choosing the scattering amplitude of an electron by an ion $\alpha_0(q)$ to correspond to a screened Coulomb interaction with $\alpha_0(q=2k_F)/\alpha_0(q=0)=0.25$. The maximum phonon wave vector $\mathbf{q}_0$ was taken equal to $2k_F$, where k_F is the radius of Fermi sphere.

For a cubic symmetry, they have taken for the anisotropy of the distribution function

$$\phi_{\mathbf{k}_d}=A_1k_\alpha+A_2(k_\alpha^3-\tfrac{3}{5}k_\alpha k^2) , \tag{7}$$

where $\alpha=x,y,z$ and A_1 and A_2 are constants which determine the relative importance of the isotropic and anisotropic terms, respectively. With these assumptions Kagan and Zhernov[12] have calculated the temperature dependence of $\eta(T)$ for different values of the ratio k_F/q_0 ($q_0=\pi b_{\min}$, where $b_{\min}$ is the nearest vector of reciprocal lattice) and for $\xi=\frac{1}{2}$. The dashed curve in Fig. 4 is obtained by Kagan and Zhernov[12] for the ratio $k_F/q_0=0.9$. A comparison between the calculated $\eta(T)$ curve and the experimental $\Delta(c,T_H)/\rho_0$ results shows that there is a relatively good agreement.

Figure 4 also shows that for large $c\sim\rho_0$ the characteristic temperature $\tilde{T}$ becomes much more strongly dependent on the concentration and rapidly shifts with the increase of c to higher temperatures, where the function $\eta(T)$ sharply decreases. Therefore, the nonlinear effects are weak in dirty samples. The cause of this nonlinear effect is the suppression of the anisotropy of the distribution function due to the elastic scattering on the impurities introduced in the samples. On the other hand, Kaveh and Wiser[3,4] have shown that the existence of the broad maximum DMR and that the $T_H \sim c^{1/5}$ Kagan and Zhernov law can be related directly to the variation of the electron distribution function from its equilibrium value.

In the high-temperature region of DMR there are some important model calculations which provide the framework for a possible explanation of the deviation. Kagan and Zhernov[11,12] attributed the linear components in $\Delta(c,T)$ to a weak coupling (interference) between the transition probabilities for electron-phonon scattering and for electron-impurity scattering. They maintained that the sign of the derivate $\rho_0^{-1} d\Delta(c,T)/dT$ would be the same as the sign of the difference between the scattering amplitudes of an electron on the impurity and the ion of the matrix, in other words, it is the same as the sign of the difference between the valencies of the ions of the impurity and the host lattice. An alternative calculation by Bhatia and Gupta[18] yields similar results. According to this calculation the interference term leads to a linear dependence of $\Delta(c,T)$ on T and the slope $\rho_0^{-1} d\Delta(c,T)/dT$ changes sign when the solvent and solute atoms are interchanged. The presents results cannot check the prediction of Bhatia and Gupta,[18] because to our knowledge there exist no experimental data on Li-Al alloys.

The present experimental results are in agreement with the simple rule of Kagan and Zhernov,[12] except for the three most concentrated Al-Li alloys, because the sign of the difference $Z_{\mathrm{Li}} - Z_{\mathrm{Al}}$ is negative. The three most concentrated alloys, as mentioned above, show in contrast to less concentrated alloys a positive DMR, which is temperature independent. This discrepancy is probably due to formation of very small Li clusters in the most concentrated alloys. The formation of these clusters leads to a change of the sign of the difference of the scattering amplitudes of the electrons by the impurities and by the ions in the matrix and so that the Kagan and Zhernov criterion can be violated. The assertion of the existence of clusters in the most concentrated alloys is also strengthened from positron-annihilation experiments,[19,20] which have shown that Al-Li alloys of the same concentration exhibit very small stable clusters of a few Li atoms.

V. CONCLUSIONS

The present measurements on dilute Al-Li alloys show that the phonon resistivity below 60 K varies as T^n where $2 \leq n \leq 5$. At intermediate temperatures the DMR $\Delta(c,T)/\rho_0$ shows a broad maximum. The temperature at which this maximum appears, shifts with impurity concentration as $c^{1/5}$. This law can be explained with the Kagan and Zhernov calculation. In the high-temperature region, the deviation $\Delta(c,T)/\rho_0$ for the alloys with small concentration depends linearly on T and has a negative slope, while the two most concentrated alloys show a positive DMR with constant slope. This behavior is attributed to the formation of very small stable Li clusters.

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