ELECTRONIC PROPERTIES OF METALS AND ALLOYS

Anomalous diamagnetism in aluminum–lithium alloys

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In the region of the equilibrium solid solutions of lithium in aluminum an anomalous low-temperature peak of diamagnetism is observed which is due to the presence of a boundary point on a line of band degeneracy directly below the Fermi level. The position and structure of the peak in the average valence function are analogous to those studied previously in the aging systems Al–Mg and Al–Zn under suitable heat treatment. The value of the lithium impurity scattering parameter for the electron states in the vicinity of the point of degeneracy mentioned is estimated, and the linear relation of that parameter with impurity-related electrical resistance in aluminum alloys is established. © *2004 American Institute of Physics.*
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INTRODUCTION AND STATEMENT OF THE PROBLEM ADDRESSED

In simple metal systems of the sp type, such as aluminum, the orbital component of the magnetic susceptibility often serves as a useful tool for diagnostics of the electronic structure, especially in cases when, because of thermal excitations or disorder in the crystal lattice, it is impossible to employ quantum oscillation or resonance methods.[1] In this case one uses the irregular behavior of the orbital susceptibility near points of electronic topological phase transitions,[2] caused by the coincidence of the Fermi level with critical energies of the electron spectrum, at which the topology of the Fermi surface changes. For example, in aluminum just below the Fermi level E_F there is a specific critical point with extremal energy E_c on a line of band degeneracy.[3] For boundary points of degeneracy of this type the electronic topological transition at $E_F = E_c$ and T, $H \to 0$, according to theoretical calculations,[3,4] is accompanied by divergence of the orbital diamagnetism on account of the interband contribution.

The corresponding peak of the anomalous diamagnetism has actually been observed[3,5] in alloys of aluminum with substitutional acceptor impurities of Mg and Zn at an average valence z of the alloy equal to the critical value $z_c = 2.945$, in the form a deep low-temperature dip, smoothed by the scattering of electrons on impurities, against the background of the appreciable paramagnetism of pure aluminum. A quantitative analysis of this feature in the behavior of the susceptibility is given in Ref. 3 on the basis of the results of a theoretical calculation of the orbital susceptibility for degenerate bands on the assumption that the disordered solid solutions of Mg and Zn in aluminum are homogeneous.

Unfortunately, in almost all binary systems of aluminum the concentration of an acceptor impurity corresponding to the average valence z_c, if it even falls in the solubility region, does so at rather high temperatures.[6] Obtaining uniform solid solutions in metastable alloys of aluminum at room temperatures requires special heat treatment with regimes that substantially influence the magnetic susceptibility of these alloys.[7] Thus the susceptibility can enrich the arsenal of tools for analysis of the mechanisms and kinetics of the accompanying structural changes. For this one needs reliable information about the behavior of the susceptibility near the diamagnetic anomaly in the system of stable solid solutions of aluminum, which can be taken as a standard, to convince oneself of its correspondence with the theoretical model, and to estimate the degree of uniformity of the solid solutions with Mg and Zn studied previously. As a candidate for the role of reference system in the present paper we have chosen the substitutional alloys of aluminum with lithium. This is the only system for which the topological transition under discussion can occur in the region of solid solutions stable at room temperature,[6,8] although the conclusions of some papers contradict that assumption.[6,9]

EXPERIMENTAL TECHNIQUE

Bars of six Al–Li alloys with concentrations $x(\mathrm{Li}) = 2$, 2.8, 3.8, 4.4, 7.4, and 10.7 at.% were melted from high-purity components: Al–5N and Li–4N. The polycrystalline samples with linear dimensions ~ 3 mm were cut out from the bars by an electrospark method, and the deformed surface was chemically etched off. The samples were subjected to a homogenizing anneal in a helium atmosphere for ~ 5 hours at a temperature of 530 °C, followed by rapid quenching in water. After the magnetic susceptibility measurements some of the samples were aged for around 3 hours at a temperature of 200 °C, and then slowly cooled at a rate of ~ 10 °C/h to room temperature, and the measurement procedure was repeated.

The susceptibility of the alloys was measured by a quantum magnetometer in a dc field of 200 Oe with an error not exceeding 5×10^{-9} e.m.u./g. The samples were placed in a

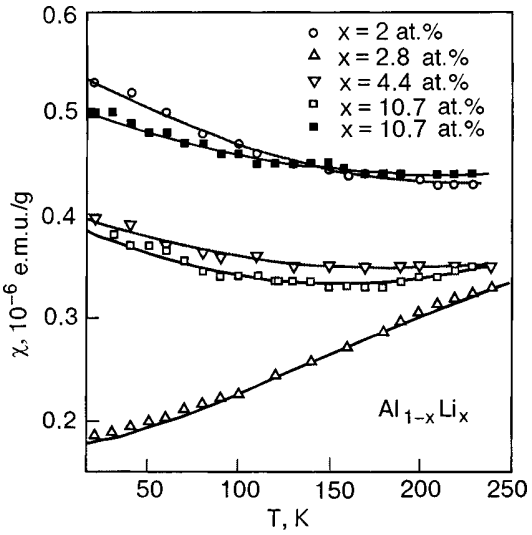

FIG. 1. Temperature dependence of the magnetic susceptibility of Al–Li alloys with different lithium concentrations (in at. %). The unfilled (□) and filled (■) squares pertain to quenched and aged samples, respectively.

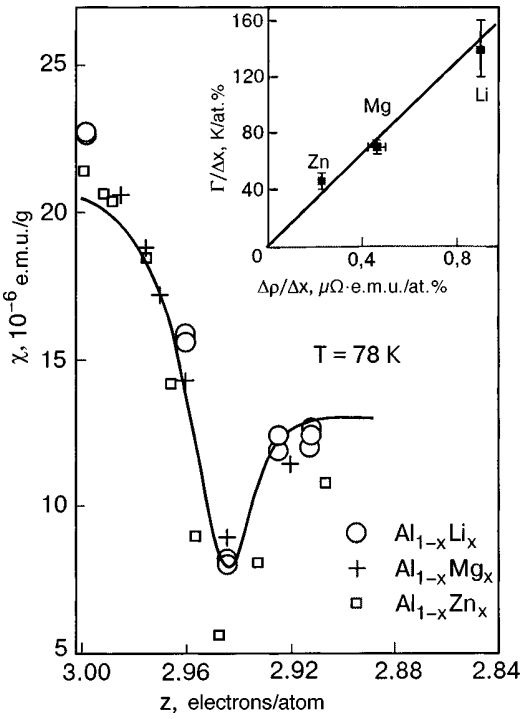

FIG. 2. Electronic part of the susceptibility of alloys of aluminum with Li (○), Mg (+) (Ref. 3), and Zn (□) (Ref. 5) at $T=78$ K versus the average valence z. The solid curve is the result of a theoretical calculation of the susceptibility of Al–Li alloys with the scattering taken into account (see text). The inset shows the relation of the impurity scattering parameter Γ to the resistivity ρ of the alloys.[8]

copper chamber in a compartment of the anticryostat and cooled by the dosed admission of cold gaseous helium into the anticryostat through a controlled valve. Together with a resistive heater on the upper part of the chamber, this system permitted regulation of the rate of cooling of the sample (usually 0.1–0.5 K/min) and the long-term maintenance of its temperature in the interval 4.2–250 K with an accuracy of ~ 0.3 K.

RESULTS OF MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Examples of the temperature dependence of the magnetic susceptibility obtained for the Al–Li alloys are presented in Fig. 1. The dependence of the susceptibility on the lithium concentration near the extremum is shown in Fig. 2. The temperature of 78 K was chosen to permit comparison with analogous data available for the alloys Al–Mg (Ref. 3) and Al–Zn (Ref. 5), which are also shown in Fig. 2. For this same reason molar units are used for the susceptibility in Fig. 2, and the ionic diagmagnetism[10] was subtracted from the measured values, the impurity concentration is expressed in terms of the average valence of the alloys, and the concentrations $x(\mathrm{Li})=2$, 2.8, 3.8, and 4.4 at. % correspond to the valences $z=2.96$, 2.944, 2.924, and 2.912.

Up to concentrations of at least 4.4 at. % Li ($z>z_c$) the susceptibility of the quenched and aged samples agrees within the limits of error of the measurements. Aging was found to have a noticeable effect only for samples with concentrations $x\geqslant 7$ at. % Li ($z=2.86$); Fig. 1. The appearance of analogous differences in the study of the quenched and aged alloys had been observed previously in the Al–Cu system[7] upon transition through the solubility boundary (<2 at. % Cu, where the average valence is still far from the critical value z_c). Thus the solubility limit of Li and Al at room temperature, which is manifested in the magnetic properties, lies in the interval from 4.4 to 7.4 at %, in accordance with the value ~ 5 at. % Li given in Ref. 8. The peak of the diamagnetism in aluminum alloys with lithium falls in the region of stable homogeneous solid solutions and is observed at the same average valence z_c as in the Al–Mg and Al–Zn systems. The amplitude of the peak almost coincides with the value found in the alloys with magnesium and is considerably lower than the amplitude in alloys with Zn, although the lithium concentration required for realization of the peak is half as high.

ANALYSIS OF THE ANOMALOUS DIAMAGNETISM

In the analysis of the experimental data presented we shall use the concepts proposed in Ref. 3 as to the nature of the irregular behavior of the magnetic susceptibility of alloys of aluminum and the expression derived there for the dependence of the susceptibility on the level of the chemical potential $\chi(\mu)$. As we have said, the decisive factor in the occurrence of the substantial dependence of the susceptibility on the concentration of an acceptor impurity is the presence in the electron spectrum A1 of a boundary point on the line of band degeneracy, lying ~ 13 mRy below the Fermi level.[3,11] The scale of that dependence allows one to neglect the influence of all other irregular contributions to the susceptibility.[3] In the calculation of the orbital anomaly in Ref. 3 it was assumed that a fragment of the electron spectrum of Al near the actual point may be satisfactorily represented by a two-band **kp** Hamiltonian, the parameters of which are expressed in terms of the known Fourier components of the pseudopotential. The theory of orbital susceptibility[12] has been adapted for the nonstandard form of the Hamiltonian obtained, and the concentration and temperature dependences of the susceptibility of Al–Zn and

Al–Mg alloys near the anomalies are described by numerical calculations with a fitting of the value of the background contribution and the scattering parameter Γ. Here the position of the level of the chemical potential (or Fermi level) in the alloys was calculated from the value of z with the use of the electronic density of states of aluminum from Ref. 11, and the scattering was simulated by the introduction of an effective temperature that depends linearly on the concentration.

From a comparison of the data obtained in the Al–Li system with experiment and with a calculation for the Al–Mg and Al–Zn alloys (Fig. 2) one can conclude that the chosen heat treatment regimes for the last two systems apparently ensure sufficient homogeneity for these solid solutions. The behavior of the susceptibility of all the alloys presented near the peak is distinguished only by the individuality of the value of the impurity scattering parameter Γ, whereas the position of the boundary point of the band degeneracy relative to the Fermi level of pure aluminum in these alloys is practically the same, $E_c - E_F(\mathrm{Al}) = (-11 \pm 2)$ mRy. Such a value follows from the true positon of the peak $z_c = 2.945$ when its shift due to the smearing at finite values of T and Γ is taken into account.[3] It is in good agreement with the value -13 mRy mentioned above.

The theoretical curve of $\chi(z)$ given in Fig. 2 for the Al–Li alloys was obtained by smearing the corresponding dependence $\chi(\mu)$ from Ref. 3 by a Lorentzian, in which the level-broadening parameter due to the scattering, $d\Gamma/dx = (160 \pm 20)$ K/at. % Li, is chosen along with the constant background component for best agreement with the measured susceptibility. The difference of the scattering parameters for impurities can be estimated directly in terms of the effective temperature from the difference of the amplitude of the diamagnetic peak in the investigated alloy systems, using for calibration the temperature dependence of the amplitudes in Fig. 1 and in Refs. 3 and 5. Along with the absolute values of the scattering parameter $d\Gamma/dx$ given in Ref. 3 for Mg (70 K/at. %) and Zn (45 K/at. %) this procedure gives for lithium impurities in Al the ratio $d\Gamma/dx(\mathrm{Li}):d\Gamma/dx(\mathrm{Mg}) \approx 1.8:1$ and $d\Gamma/dx = 120 \pm 20$ K/at. %. The temperature dependence of the susceptibility expected for this parameter at the extremum agrees with experiment (the sample with 2.8 at. % Li in Fig. 1). For estimation we take the average value $d\Gamma/dx \approx 140$ K/at. % Li, bearing in mind the approximate nature of both methods of determining this quantity. For example, at the edge of the dependence $\chi(x)$ the region of averaging of the susceptibility over energy at the value obtained for Γ goes beyond the domain of applicability of the two-band model, [3] there exists some difference in the scattering parameter estimated using a Lorentzian and an effective temperature,[3] and in the calculation of $\chi(T)$ for the alloys the unknown temperature dependence of the level of the chemical potential μ is ignored. Eliminating these defects, which, as can be seen from the results, are not fundamental, would require considerable complication of the calculation, which is not justified at this stage.

The inset in Fig. 2 shows the relation between the values of Γ in the alloys under discussion with the influence of those impurities on the resistivity ρ of aluminum.[8,13] It turns out to be linear to within the error limits. The smallest scattering, strangely, is caused by zinc and not magnesium which is next to aluminum in a row of the periodic table. As a consequence of the fact that for the electron scattering processes governing the susceptibility anomaly the initial states are well localized in **k** space near the singular point, one can make a quantitative estimate of the scattering parameter, and the aforementioned strangeness in the influence of Zn and Mg can be linked to differences in the details of the structure of their pseudopotential form factors.[3]

CONCLUSION

This study has shown that the region of solubility of lithium in aluminum at room temperature, determined from the magnetic properties, exceeds 4.4 at. % and includes an electronic topological phase transition associated with the boundary point of a line of band degeneracy in the electron spectrum of Al. The peak of anomalous diamagnetism corresponding to the transition in stable homogeneous solid solutions of Al was realized for the first time. These reference data confirm the reliability of the form of the anomaly observed in the aging Al–Zn and Al–Mg alloys after a special heat treatment and its agreement with the theoretical model. The value of the electron scattering parameter for a lithium impurity near the boundary point was determined, and it was established that this parameter is linearly related to the resistivity of the alloys. On the basis of the available data, one can use the susceptibility for quantitative analysis of effects due to the influence of structural transformations in aging aluminum alloys on the degenerate electron states and establish the characteristic times and mechanisms of such transformations.

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