Thermo-emf anomaly in lithium-magnesium alloys

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(Submitted 25 March 1982)

Pis'ma Zh. Eksp. Teor. Fiz. **35**, No. 9, 375–377 (5 May 1982)

The thermo-emf of 12 specimens was measured in the range of concentrations x: 0–40 at.% Mg. A sharp increase in the magnitude of the thermo-emf was observed at $x_c = 0.2$. The positive sign of the anomaly corresponds to contact of the Fermi surface with the face of the Brillouin zone.

PACS numbers: 72.15.Jf

Interest in the change of the topology of the Fermi surface, accompanying a smooth change in some parameter, for example, the pressure or impurity concentration, has greatly increased after Lifshitz's work.[1] He predicted that the kinetic coefficients of the metal at the transition to a new topology (formation or rupture of bridges, appearance or disappearance of voids) must have singularities of the form $|z|^{1/2}$ or $|z|^{-1/2}$, where z is the parameter expressing the proximity to the transition, proportional, for example, to the difference between the pressure and the critical pressure ($z = 0$ at the transition point). In Ref. 1, such transitions were classified as 2½-type transitions. The study of 2½-type transitions in alloys is of special interest. Here, it is generally possible to vary the electron concentration over a wide range, but on the other hand, it has been repeatedly stated that singularities cannot be observed in this particular case, since the quasimomentum and Fermi surface are not formally defined in disordered alloys.[2]

In a recent paper,[3] the electrical resistance and thermo-emf were calculated for a 2½-type transition in the alloy $Li_{1-x}Mg_x$, both components of which Li and Mg, are well

 0021-3640/82/09462-04$01.00

described with the help of the theory of the pseudopotential.[4] The theoretical concentration dependences, obtained without any assumptions concerning the diffuseness of the Fermi surface, have clearly distinguished anomalies. It was shown that the anomaly in the thermo-emf is much stronger than in all other kinetic coefficients. In spite of the extensive literature devoted to different physical investigations of LiMg alloys, there are no experimental data on the resistance and thermo-emf as a function of concentration.

LiMg alloys form a continuous series of solid, disordered solutions with a *bcc* structure up to $x = 0.7$ with comparatively small changes in the interatomic distances,[5,6] and it was reasonable to expect here a 2½-type transition or else two. Different researchers have measured Hall's emf[7] and the magnetic susceptibility,[8] optical properties,[9] positron annihilation,[10] and the Knight shift.[11] For various reasons, the transition point was assigned values from $x_c = 0.19$ to $x_c = 0.50$, but no clearcut anomaly was observed. The situation in LiMg alloys is rather complicated because in these alloys, as in pure lithium, there is a martensite transformation, which never proceeds to completion, so that below some temperature M_s there is a mixture of two phases: *bcc* and *hcp*. In pure lithium, $M_s = 70$ K. For this reason, most investigations were carried out at liquid nitrogen and higher temperatures in order to focus attention only on the *bcc* phase. However, as x increases, M_s increases rapidly,[12] and for $x = 0.12$ we find $M_s = 125$ K,[13] so that actually at the liquid nitrogen temperature, there is a mixture of two phases at nearly all concentrations ($x \geqslant 0.02$), while for intermediate concentrations ($x > 0.1$), the ratio of the *bcc* and *hcp* phases generally changes little toward low temperatures. For this reason, it was interesting to carry out measurements for helium temperatures as well, where it is possible to distinguish quite clearly the electron part of the thermo-emf.

LiMg alloys were prepared in an induction furnace in a pure argon atmosphere using a crucible-free method, which provided uniform mixing of the alloy and then its rapid cooling. Specimens used for the measurements consisted of pieces of wire ~35 mm in length and ϕ 0.6 mm, obtained by extruding part of the rod through a draw plate. The magnesium concentration x was determined from the starting charges. In addition, all specimens, and more precisely the parts of the ingots from which the specimens were obtained, were chemically analyzed. The data from this analysis agree well with the computed data (see Fig. 1). All procedures with specimens were carried out in an atmosphere of argon and helium.

The resistance ratio $\rho_{300}/\rho_{4,2} = 700$ for the starting Li and ~300 for Mg. For the control "alloy" Li without additions of Mg, this ratio amounted to ~400. The thermo-emf of the specimens was measured by the differential method relative to pure lead, for which the data in Ref. 14 were used. The potential difference was measured using a R363-3 potentiometer with sensitivity $\sim 10^{-8}$ V. In order to decrease the effect of drift on the zero point, the measurements were made with commutation of the heat flow.

The results of the measurements are shown in Fig. 1. Curve 1 shows the concentration dependence of the residual resistance $\rho_{4,2}/\rho_{300}(x)$. The dependences $\rho_{300}(x)$ and $\rho_{4,2}(x)$ separately have a much higher spread, due to the imperfection of the geometry of the specimens. The two lower curves 2 and 3 correspond to measurements of the thermo-emf. The continuous curve 2 is a result of the measurements at helium temperatures $T = 2$–7 K, where the dependence $\alpha(T)$ within the limits of error could be approximated by straight lines, and the value of the point on the curve 2 is the average slope.

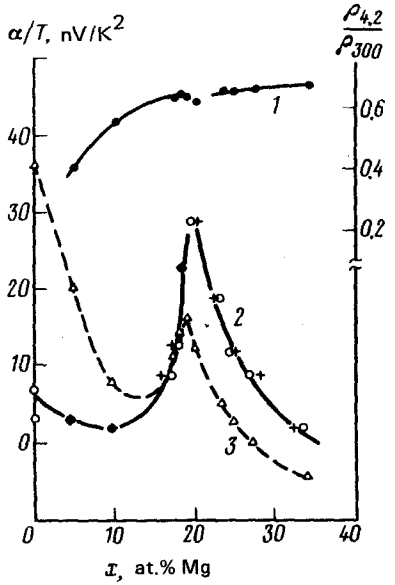

FIG. 1. Residual resistance (1) and thermo-emf of $Li^{I}_{1-x}Mg_x$ alloys (2 and 3) as a function of x, the concentration of Mg in at.%. The scale for curve 1 is indicated in the upper right and for curves 2 and 3 on the left. The continuous curve 2 corresponds to measurements at helium temperatures (see text). The dashed line 3 corresponds to measurements at $T = 78$ K. The magnitude of the error along the ordinate axis for all curves corresponds to the size of the points.

The circles correspond to the computed value of the concentration x and the crosses correspond to the results of the chemical analysis. Of the two points at $x = 0$, the lower point is pure lithium and the upper point is the control alloy without magnesium. The dashed line connecting the traingles is $\alpha_{78\,K}(x)/78$ K. At $x_c = 0.2$, a sharp anomaly is observed in curve 2. To the left of the maximum, the shape of the curve agrees well with that predicted theoretically,[3] but instead of the sharp cutoff in Ref. 3 to the right of the maximum, there is a gentle decline. At nitrogen temperatures, curve 3, the anomaly is easily noticeable, but a strong monotonic component $\alpha(x)$ is superimposed on it, stemming, apparently, from the phonon contribution to the thermo-emf, which at room temperature is much larger. On curve 1 at $x \sim 0.2$, some nonmonotonicity is also noticeable, exceeding the limits of the experimental error, but this curve is the result of dividing two dependences $R_{4,2}(x)$ and $R_{300}(x)$, so that it is difficult to interpret it. The magnitude of the residual specific resistance at $x = 0.2$–0.3 is $\sim 2 \times 10^{-5}$ $\Omega \cdot$ cm.

It follows from the nature of the dependences $\alpha(x)$ observed that the diffuseness of the Fermi surface of the face of the Brillouin zone in disordered alloys could be small enough, so that the 2½-type transition would be manifested very clearly. The positive sign in the $\alpha(0.2)$ spike is attributed to the fact that at $x_c = 0.2$ the Fermi surface forms a contact with the face of the Brillouin zone. However, there are as yet not enough data to establish uniquely whether or not the contact in the *bcc* phase is observed, as is shown in Ref. 3 (where the theoretical value $x_c = 0.25$, which agrees well with our experiment) or the anomaly is related to contact with the *hcp* phase. We should also note the strong x dependence of the phonon component of the thermo-emf α^{ph}, caused by entrainment. For small x, α^{ph} is large and has a positive sign. As x is increased, α^{ph} decreases rapidly, and then, apparently, changes sign.

We thank N. A. Chernoplekov for interest in our work, V. G. Vaks for discussions

of the results, and also G. É. Karstens, N. A. Babushkina, E. V. Mel'nikov, S. V. Varyukhin, and É. G. Chudinov for their help.

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Translated by M. E. Alferieff
Edited by S. J. Amoretty