ELECTRICAL RESISTIVITY OF LIQUID BINARY ALLOYS EXHIBITING A MISCIBILITY GAP*

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(Received 14 August 1970)

We have made detailed measurements of the variation of the electrical resistivity in the vicinity of the critical temperature and composition of the liquid alloys Hg-Ga and Bi-Ga. Anomalies are observed in the temperature dependence of resistance at up to 10°C above the critical temperature in the Bi-Ga system and up to 2°C in the Hg-Ga system.

Critical phenomena in binary liquids have been the subject of many investigations.[1] The observation of critical opalescence and acoustic absorption in nonmetallic binary liquids exhibiting some range of immiscibility has indicated that, in the vicinity of the consolute temperature, fluctuations in concentration occur. Binary alloys which exhibit a miscibility gap in the liquid phase might also be expected to exhibit concentration fluctuations in the region of the critical temperature and composition. Since the nature of the interatomic forces in metals and nonmetals is different, a comparison of critical behavior in these systems could provide insight into the effect of interatomic forces on critical phenomena.

The large absorption of light by metals precludes the use of optical-scattering techniques which have proved so effective in nonmetallic systems. However, x-ray- and neutron-scattering experiments have been performed, although they are apparently somewhat less sensitive than the optical technique. The Na-Li system was studied by Brumberger et al.[2] using x rays, while Bi-Zn, Pb-Ga, and Bi-Ga alloys were studied by Wignall and Egelstaff[3] using neutrons. In both cases the data were interpreted as demonstrating the existence of critical opalescence in binary liquid-metal mixtures. The x-ray or neutron structure factor enters into the simple formula for the electrical resistivity[4] of a liquid conductor in a very direct way. It is, hence, of interest to determine the extent to which the additional scattering assumed to arise from concentration fluctuation affects the resistivity. This Letter presents detailed measurements of the electrical resistivities as a function of temperature and composition of the liquid alloys Bi-Ga and Hg-Ga.

The data were obtained by a simple dc four-probe potentiometric technique. The system was designed to allow the detection and elimination of gas bubbles formed from adsorbed gases, and of inhomogeneities in composition. It consists of a vertical Pyrex capillary tube about 0.05 cm diam and 10 cm long suspended in the liquid alloy. A current of about 10 mA was passed through the alloys in the capillary, which allowed a potential difference of tens of millivolts to be developed across the capillary while keeping the current density well below the values required for the observation of mass transport effects. The potential was measured to 0.5 μV by a Leeds and Northrup K3 potentiometer. Temperatures were determined by means of thinly sheathed Pt-Pt/13% Rh thermocouples also immersed in the liquid. Details of the apparatus and the sensitivity of the technique are given elsewhere.[5]

Alloys of the critical composition[6] were prepared from weighed amounts of Bi (99.9995% purity), Ga (99.999% purity), and Hg (99.99% purity) obtained from the Leytess Metal and Chemical Corporation. Composition changes were made by adding known amounts of a component to the mixture. Previous experience[5] has indicated that inhomogeneities in alloy composition may exist even at over a hundred degrees above the liquidus temperatures, so great care was taken to ensure proper mixing of the alloys. During a run, temperature-change rates did not exceed 2°C/h.

Results which are typical of many Hg-Ga alloys studied in the vicinity of the critical composition are shown in Fig. 1. In this system the critical temperature is given as 204°C and the critical composition is Hg-50 at.% Ga.[6] The surprising result is the appearance of a minimum in the resistance with decreasing temperature. The 0.1% bar illustrates that the effect is really quite small. The increase of resistance with decreasing temperature after the minimum is passed is readily understood, even though the liquidus curve of this system is quite symmetric. It is characteristic of mercury alloys that the composition dependence of resistance becomes stronger with increasing mercury concentration.[7] Hence as the temperature is decreased in the two-phase region, the resistance increase associated with the mercury-rich component is not entirely compensated by the decrease in resistance of the gallium-rich component. The

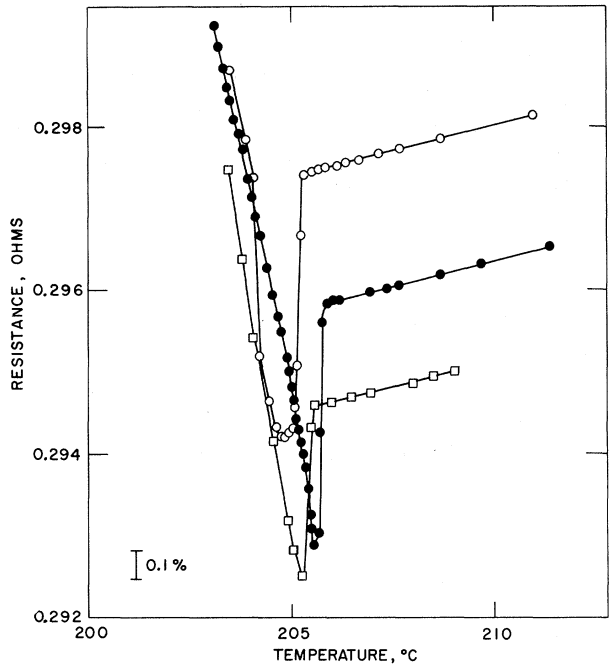

FIG. 1. The variation of resistance as a function of temperature of three Hg-Ga alloys in the vicinity of the critical composition (Hg-50 at.% Ga). The critical temperature is reported to be 204°C (see Ref. 6).

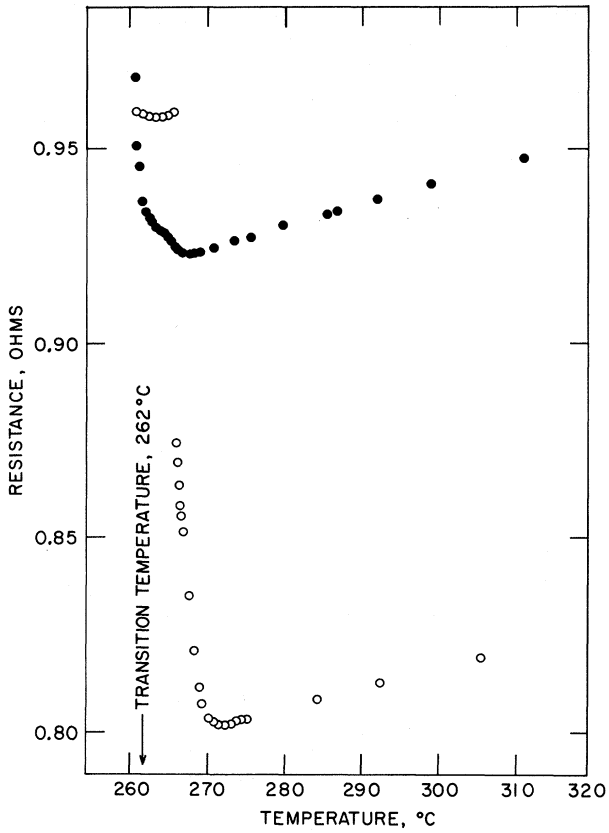

FIG. 2. The variation of resistance as a function of temperature of two Bi-Ga alloys in the vicinity of the critical composition (Bi-70 at.% Ga). The critical temperature is given as 262°C (see Ref. 6).

total resistance therefore will increase with decreasing temperature, as is observed.

It might be expected that the resistance of a system in which concentration fluctuations occur would increase. However, it should be realized that the measured resistance is an average of several competing effects. Concentration fluctuations themselves may well give rise to extra scattering, but the scattering within a region of given concentration may have either increased or decreased from that of the homogeneous alloy of average concentration. The net effect could then be either a decrease or an increase in resistance. The latter effect is illustrated in Fig. 2, in which results for two compositions in the Bi-Ga system are shown. Similar data taken at many other compositions have been omitted for clarity. Behavior that is characteristic of a homogeneous liquid alloy is observed for all alloys above 272°C. However, below this temperature a rapid increase in resistance is observed with decreasing temperature. Results in this system were not consistently reproducible so it was not possible to obtain reliable values of the temperature coefficient of resistance in the transition region.

These measurements indicate that the resistivities of binary alloys which exhibit a miscibility gap display characteristics which may be attributed to a manifestation of critical-concentration fluctuations. However, it is evident that further experimental work is required to establish resistivity behavior fully at this type of transition. Since resistivity is a strong function of concentration even in homogeneous alloys, a careful theoretical analysis will be required to establish an understanding of the usual critical parameters.

It is a pleasure to thank Dr. J. E. Enderby for stimulating my interest in this problem.

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*Work performed under the auspices of the U. S. Atomic Energy Commission.

[1]See, for example, *Critical Phenomena, Proceedings of a Conference, Washington, D. C., 1965,* edited by M. S. Green and J. V. Sengers, National Bureau of Standards Miscellaneous Publication No. 273 (U. S. G. P. O., Washington, D. C., 1966).

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[5]P. D. Adams and J. S. Ll. Leach, Phys. Rev. 156, 178 (1967).
[6]See the respective phase diagrams given by R. P. Elliot, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1965), 1st suppl.
[7]P. D. Adams, Phys. Rev. Lett. 20, 537 (1968); and also reported in N. W. Ashcroft and D. C. Langreth, Phys. Rev. 159, 500 (1967).

THEORY OF SOFT OPTIC MODES AND PHASE TRANSITIONS IN β-W STRUCTURE TRANSITION-METAL ALLOYS*

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(Received 1 May 1970)

A calculation of the phonon frequencies of the β-W structure crystals shows that long-wavelength optic-mode instabilities occur. These are associated with a high density of electronic states in the transition-metal d bands. The $\Gamma_{15}^{(-)}$ and $\Gamma_{25}^{(-)}$ optic modes soften: these are consistent with a second-order structural phase transition.

Soft optic modes have been proposed[1,2] as underlying the structural phase transition,[3,4] and other anomalous properties[5] of the β-W compounds V_3Si and Nb_3Sn, including possibly their transition to the superconducting state.

In this Letter we report on a theoretical mechanism for such optic-mode softening. We find that when the Fermi level falls in a region of large electronic density of states, the long-range bare-ion Coulomb potentials are overscreened and two $\vec{q}=0$ optic modes are destabilized. These are two of the three modes which the Landau theory permits to be order parameters in a second-order structural phase transition.[2] The remaining optic modes are stable.

The calculation of the phonon spectrum makes use of the adiabatic harmonic approximation, and is for zero temperature ($T=0$). Results for $T>0$ will be published elsewhere. We have used the linear chain model[6,7] for the d-band states, and we have assumed that the Fermi level falls within the d bands, and that transitions to other bands (s, p, etc.) can be neglected or can be included in an effective charge for the ions.[8]

The long-range-force contributions to the dynamical matrix[9] have been accounted for by using bare-ion Coulomb potentials screened by the wave-number-dependent, zero frequency, self-consistent-field dielectric function, computed for scattering within the d bands in the diagonal screening tensor approximation.[8-10] The details of the calculation are given in Ref. 8. In computing the dielectric function, matrix elements involving the d-band Bloch functions are required.[10] We have constructed these Bloch functions from atomic d functions of the form

$$\Phi_m^d = R(\lambda) Y_{2m}(\theta, \varphi), \tag{1}$$

where

$$R(\lambda) = \tfrac{2}{3}(2\lambda^7/5)^{1/2} r^2 e^{-\lambda r} \tag{2}$$

with λ a free parameter determining the range of the d-state Bloch functions, and $Y_{2m}(\theta, \varphi)$ a spherical harmonic.

In Fig. 1 we illustrate the linear chain or nearest-neighbor tight-binding model d-band energies.[6] The ξ_m are related to atomic overlap integrals, k is one of the three Cartesian components of the wave vector, and a is the lattice constant. There are three degenerate sets of one-dimensional-like d bands corresponding to the three coordinate (chain) directions.

The adjustable parameters in the theory are ξ_0, ξ_1, ξ_2, Z_A, Z_B, E_F, and $\lambda a = \sigma$. Here the Z's are the bare ionic charges, and E_F is the position of the $T=0$ Fermi energy within the d bands.