Gravitational Separation and Resistance Anomalies in Liquid Binary Alloys with Miscibility Gaps

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(Received 21 December 1970)

The questions of anomalies in the electrical resistivity and meniscus motion near the critical point of a binary metallic liquid with a miscibility gap are investigated from an experimental standpoint as well as from a simple model calculation.

A recent paper by Adams[1] reported anomalies in the electrical resistivity of liquid binary alloys with a miscibility gap, notably in the systems Ga-Hg and Bi-Ga. There is no definite explanation given for the anomalies observed, which were of the order of 1% of the resistivity in one system and about 20% in the other. In a series of measurements to establish the critical exponent of phase separation in the metallic binary systems Ga-Hg[2] and Li-Na,[3] we have observed similar effects which we can definitely ascribe to the motion of the level (or meniscus) between the two phases below the critical temperature.

The sample cells used in the electrical resistivity experiments consisted of a 9-mm i.d. Pyrex tube for the Ga-Hg mixtures and a welded 12-mm i.d. stainless-steel tube for the Li-Na mixtures. Both cells were equipped with evenly spaced electrodes—tungsten wires sealed in the Pyrex tube and copper wires hard-soldered to the outside of the stainless-steel tube. The tubes, containing weighed amounts of the appropriate constituents, were housed in a calorimeter, which in turn was situated in a vertical tubular furnace. With this arrangement it was possible to maintain the temperature constant to within 0.05°C over the full length of the sample. The temperature was monitored with a series of Alumel-Chromel thermocouples which were in contact with the sample cells.

Each cell and its contents was brought to a temperature of about 80°C above the pertinent transition temperature and stirred until the ratio of the resistivities of the different sections of the tube did not change any more. The temperature was then lowered slowly and the resistances of some or all the sections of the sample were continuously monitored. Figure 1 shows typical results for a critical mixture of Ga-Hg where we have plotted the resistances of four different sections divided by the resistances at the critical point, R_c, versus the temperature. This normalization procedure was necessary because the geometrical factors of the different sections agreed only to within about 15% because of the difficulty in manufacturing the measuring cell. The cooling rate was approximately 25°C/hr. Sections 1 and 2 were Hg rich and the resistivities were identical throughout the experiment. Section 4 was Ga rich and its resistivity agreed with sections 1 and 2 only above T_c, departing from them very drastically below T_c. Section 3 was identical to the other sections only above T_c while below T_c it showed behavior intermediate between section 4 on one hand and sections 1 and 2 on the other hand. This behavior implies that section 3 contained the meniscus between the Ga-rich and the Hg-rich layers. Repeating the measurements on sections 2 and 4 near the critical temperature with a cooling rate ten times slower

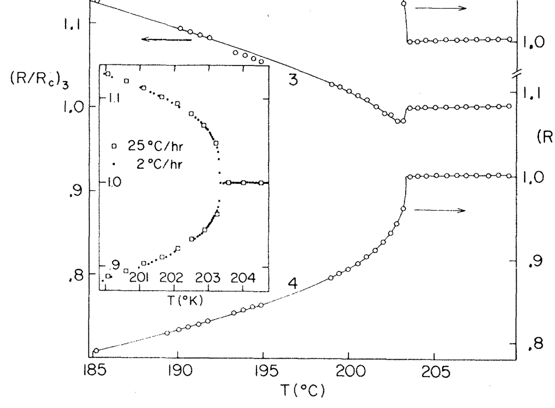

FIG. 1. Normalized resistivities of four consecutive sections of a mixture of Ga—50 at.% Hg near the critical temperature. Inset: influence of cooling rate on measured resistivities.

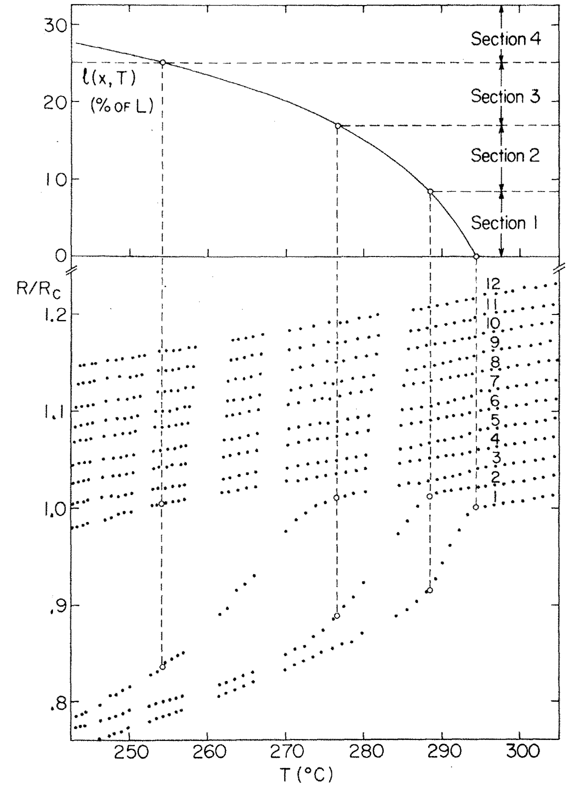

FIG. 2. Normalized resistivities of twelve consecutive sections of a mixture of Li–18.5 at.% Na versus temperature. The different curves are vertically displaced. Top: calculated position of the interface between the Li-rich and the Na-rich layer, l (18.5, T), according to Eq. (4).

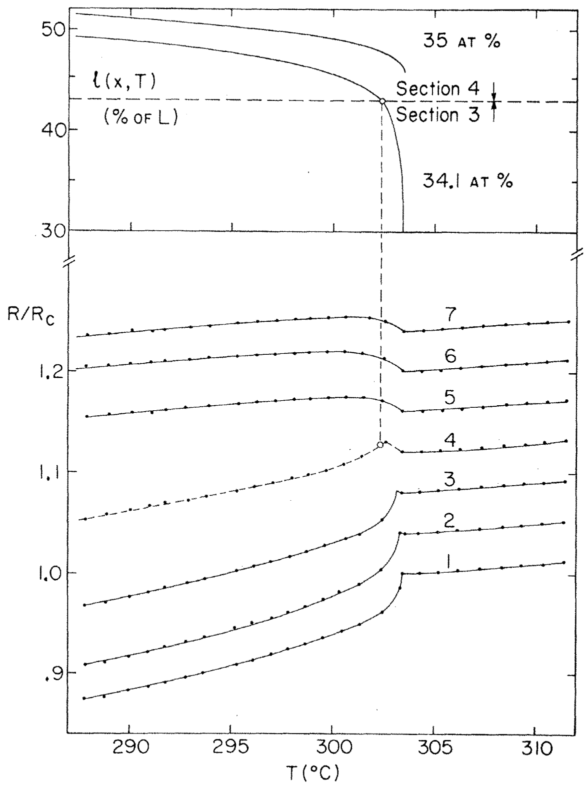

FIG. 3. Normalized resistivities of seven consecutive sections of a mixture of Li–34.1 at.% Na versus temperature. The different curves are vertically displaced. Top: calculated position of the interface between the Li-rich and the Na-rich layer, l (34.1, T) for this sample and l (35.0, T) for a sample of critical composition, according to Eq. (4).

duplicated exactly these results, also shown in Fig. 1. The gravitational separation of these layers is thus very fast and we are indeed observing the system under equilibrium conditions.

With a sample of composition far enough from the critical composition, the motion of the meniscus may be followed through a number of sections. Figure 2 shows data on a mixture of 18.5 at.% Na in Li (the critical composition is near 35 at.% Na in Li).[3-6] The twelve sections measured behave the same way above T_c (~294.2°C); at any temperature below T_c they fall into three groups: a group of "lower" sections (or Na-rich sections), a group of "upper" sections (or Li-rich sections), and a single section which we may call the meniscus section. By looking at plots like Fig. 2 we were always able to monitor the position of the meniscus at a given temperature. It is easily seen that the motion of the meniscus is most rapid in the vicinity of the critical temperature and anomalies such as those reported by Adams[1] occur. In our experiments on Li-Na mixtures, we found "dips" such as those of Adams's Fig. 1 and of our Fig. 1, layer 3, or "bumps" such as layer 4 of Fig. 3 for a sample of 34.1 at.% Na in Li. The significant fact is that in both systems studied, and at all temperatures, the resistivities of all the sections could always be grouped in the manner described above. Thus we are convinced that we really see only the effects of a moving meniscus, especially since the direction of its initial motion can always be predicted for a given sample once the critical composition is known.[7] The meniscus will move, even for samples of exactly critical composition, where it forms near the middle of the tube, as long as the curve of density versus composition is not horizontal in the region of composition spanned by the two layers. The latter condition has extremely little chance of being fulfilled in a binary system where the densities of the two constituents differ by a factor of 2 or 3.

For the purpose of our discussion there are two important differences between the systems considered:

(1) In the Ga-Hg system the denser layer (i.e., the Hg-rich layer) is more resistive than the less dense layer, whereas in Li-Na the less dense layer (i.e., the Li-rich layer) is more resistive than the denser layer; thus the reversed numbering of the sections in Fig. 1 relative to Figs. 2 and 3.

(2) In the Ga-Hg system the resistivity R increases monotonically with composition when going from pure Ga to pure Hg and $d^2R/dx|_{T>T_c} > 0$ (where x is concentration of Hg); in the Li-Na system $d^2R/dx^2|_{T>T_c} < 0$ for all x and there is a maximum in resistivity at about 22.5 at.% Na.[3] This explains why Sects. 1-3 of Fig. 1 keep increasing while Sects. 5-7 of Fig. 3 turn around, and why Sects. 5-12 of Fig. 2 never increase at all.

We demonstrate the motion of the meniscus for the Li-Na system, where accurate data on density versus composition are available in the temperature region of interest.[4,5] The density near T_c in the Li-Na system is given (to within 1%) by the equation

$$\rho(x) = 0.496 + 0.610\times 10^{-2}x - 0.244\times 10^{-4}x^2 \quad (\mathrm{g/cm^3}), \tag{1}$$

where x is in at.% Na and the small temperature dependence is neglected. The phase-separation curve is assumed to follow the equation[8]

$$|x_c - x| = A^{\pm}(T_c - T)^{1/3} \tag{2}$$

with $x_c = 35.0$ at.% and $T_c = 303.5$°C. The two branches go through the points (19.3, 295.5) and (54.0, 295.5), from which we deduce

$$A^- = 15.7/2 = 7.85$$

and

$$A^+ = 19/2 = 9.50, \tag{3}$$

where A^- is for the branch with $x < x_c$ and A^+ is for the branch with $x > x_c$. With these equations we can determine the position of the meniscus in a cylinder of constant cross section at all temperatures. We can neglect the small thermal-expansion term of the homogeneous mixture for $T > T_c$ or for the homogenous layers for $T < T_c$ and assume the length of the column L_0 of liquid alloys to be constant. The fractional length of the column of Na-rich liquid at a temperature $T < T_c$ and an overall Na concentration of x is given by

$$l(x,T) \equiv \frac{L(x,T)}{L_0} = \frac{[\rho(x) - \rho(x^-)]}{[\rho(x^+) - \rho(x^-)]}, \tag{4}$$

where $x^{\pm}$ are the solutions of Eq. (2). The top curves in Figs. 2 and 3 show the behavior of $l(x, T)$ as a function of temperature for the appropriate composition. Also given in Fig. 3 is the motion of the meniscus for a sample of exactly critical composition. As can be seen, the change of the level in the initial $\frac{1}{2}$°C below T_c amounts to more than 3% of the total height of the liquid column. The fact that it does not start out at exactly the middle is a reflection of the asymmetry in the A's, Eq. (3). Any nonuniformity in cross section over the whole sample length will have an influence on the precise motion of the meniscus; in the experimental situation used by Adams[9] the motion is amplified and it is easily conceivable that the meniscus moved past one of the voltage leads to the active part of the sample which was contained in a capillary, thus accounting for the sharp dip.

In conclusion, we have demonstrated that metallic binaries with miscibility gaps in the liquid state separate gravitationally very fast at the temperature of phase separation. We have shown experimentally that the interface between the layers moves vertically below T_c, even for samples of exactly critical composition, in quantitative agreement with the predicted behavior. This motion leads to the resistance anomalies observed in the present work, and, presumably, also to those observed by Adams.

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[1] P. D. Adams, Phys. Rev. Lett. 25, 1012 (1970).

[2] H. K. Schürmann and R. D. Parks, Phys. Rev. Lett. 29, 367 (1971).

[3] H. K. Schürmann and R. D. Parks, unpublished.

[4] F. A. Kanda, R. C. Faxon, and D. V. Keller, J. Phys. Chem. Liquids 1, 61 (1968).

[5] R. C. Faxon, thesis, University of Syracuse, 1966 (unpublished).

[6] The phase diagram for Li-Na as given in *Constitution of Binary Alloys, First Supplement,* edited by R. P. Elliott (McGraw-Hill, New York, 1965), has been shown to be in error by two independent investigations (Refs. 3-5) using three different techniques. See discussion in Refs. 4 and 5.

[7] Whether we observe a "dip" or a "bump" depends only on whether the denser layer is more or less resistive than the less dense layer.

[8] For the sake of this argument it is not relevant whether the numbers quoted are really exact; especially the exponent in Eq. (2) does not necessarily have to be $\frac{1}{3}$. Experimental evidence that the exponent is close to $\frac{1}{3}$ for the Ga-Hg system is presented in Ref. 2.

[9] P. D. Adams and J. S. Ll. Leach, Phys. Rev. 156, 178 (1967).