

Specific-Heat Anomaly of a Metallic Binary Liquid with Miscibility Gap*

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An anomaly in the specific heat c_p of liquid Ga-Hg near the critical point of phase separation is observed and found to resemble that measured in nonmetallic binary systems. The singular part of c_p has a temperature dependence $c_p \approx [(T - T_c)/T_c]^{-\alpha} = \epsilon^{-\alpha}$, with $\alpha = 0.3 \pm 0.1$ in the reduced temperature interval $5 \times 10^{-5} < \epsilon < 2 \times 10^{-2}$.

I. INTRODUCTION

In a recent paper¹ we reported the critical exponent β of phase separation for the metallic binary system gallium-mercury. It was somewhat surprising that we could not see any precursive behavior of the resistivity above T_c ,² since we had the capability of measuring changes as small as one part in 10^5 . Since it is well established³ that near critical points in metallic systems (e. g., ferromagnetic,⁴ antiferromagnetic,⁵ and order-disorder⁶ transitions) the specific heat shows a singularity similar to that shown by the temperature derivative of the resistivity, we decided to check whether the specific-heat anomaly could be detected in the Ga-Hg system. We present here data on what we believe are the first measurements of the critical specific heat of a liquid metallic system.⁷ We have shown elsewhere⁸ that paraconductivity is observable in other binary metallic liquids (notably Li-Na and Bi-Ga) and have given an heuristic argument why it might not be measurable in the Ga-Hg system.

II. PREVIOUS WORK ON NONMETALLIC SYSTEMS

The critical exponents α^\pm are defined by the relation

$$c_p^\pm = c_p^{0\pm} + \frac{c^\pm}{\alpha^\pm} [|(T - T_c)/T_c |]^{-\alpha^\pm} = c_p^{0\pm} + \frac{c^\pm}{\alpha^\pm} |\epsilon|^{-\alpha^\pm}, \quad (1)$$

where the superscripts + and - refer to the temperature being higher or lower than the critical temperature and $\alpha = 0$ corresponds to a logarithmic singularity. Previous measurements of c_p in immiscible liquids have been done only on systems with the critical temperature near room temperature or at cryogenic temperatures and therefore never on metallic systems. Schmidt *et al.*⁹ measured the heat content of $\text{CCl}_4\text{-C}_7\text{F}_{14}$ with an ice calorimeter and they deduced c_p by graphical methods. At $T < T_c$ their sample was not stirred: The influence of stirring on the total heat capacity in the heterogeneous region is discussed in Sec. III. The data by Schmidt *et al.* were subsequently compared to the specific heat as calculated by Fixman,¹⁰ who gets $\alpha^+ = \frac{1}{2}$, but this power law is built into the

theory (see the review article by Egelstaff and Ring,¹¹ who calculate $\alpha^+ < 0.3$ for the data by Schmidt *et al.*⁹).

Skipov and Kostin,¹² on the other hand, measured c_p in the triethylamine-water and triethylamine-deuterium oxide systems [$(\text{C}_2\text{H}_5)_3\text{N-H}_2\text{O}$ and $-\text{D}_2\text{O}$, respectively], which have lower consolute temperatures. They measured the specific heat with a pulse method and kept the sample stirred at all temperatures. Their data were later analyzed with the determination of α in mind by Blagoi and Gusak,¹³ who found $\alpha^\pm = 0.2$ for both systems in the reduced temperature range $10^{-4} < \epsilon < 2 \times 10^{-2}$. The uncertainty in α^\pm , however, was quite large, as it almost always is for liquid systems, and $0.1 < \alpha^\pm < 0.25$ is compatible with their data.

Brouwer *et al.*¹⁴ measured the specific heat of liquid mixtures of neon and hydrogen over the whole concentration range of phase separation. They analyzed one sample of critical composition for the exponent α^+ and got $0 < \alpha^+ < 0.2$ (the sample was stirred in the heterogeneous region). In the $\text{He}^3\text{-He}^4$ system there does not appear to be a divergence in the specific heat at the critical composition for temperatures $T \rightarrow T_c^+$; in this system the λ transition, which is taking place at the same temperature, must influence the very character of the transition.¹⁵

III. EXPERIMENTAL METHOD

The sample, which contained 49.74-at. % Hg, consisted of 8.7385-g gallium (99.999% pure, from Eagle-Picher Co.) and 24.8805-g mercury (99.99999% pure, from Beckman Instruments). It filled about 7.5 cm of a Pyrex tube of 10-mm o. d. and 8-mm i. d. which had been provided with a reentrant thermocouple well of 3-mm-o. d. 1.8-mm-i. d. Pyrex tubing, 5 cm long. The sample tube with the metals inside was sealed off under vacuum; the mass of the glass tube was determined to be 8.3320 g. A heater of 0.2-mm-diam Nichrome wire was wound the length of the liquid column and had a room-temperature resistance of 11.5 Ω .

This assembly was placed in a calorimeter which in turn was inserted in a tube furnace mounted such that it could be turned by 180° around an axis perpendicular to the tube axis, thus inverting the Py-

rex tube with the sample. The thermocouple well contained a differential thermocouple junction of 0.05-mm-diam Alumel-Chromel wires sheathed in ceramic, the other junction being at calorimeter temperature, which was measured with another Alumel-Chromel thermocouple of 0.3-mm-diam wire. Before every run the sample was brought to a temperature well above T_c ; the whole assembly was then inverted repeatedly to mix the sample while the temperature difference between calorimeter and sample was monitored. The initial inversion caused the sample temperature to drop about 10°C but it mixed readily, i. e., after about 15 inversions the temperature did not change on subsequent inversion.

It is not clear at all whether, in the heterogeneous phase, the mixture should be kept stirred or not. There are various arguments against stirring the mixture: (i) The stirring process is equivalent to an additional heat input and this is hard to calibrate or to keep constant.¹⁴ (ii) If the separation of the two phases is as fast as it seems to be in the two systems we measured by the resistivity technique,^{1,2} one could hardly expect to keep the sample in a homogeneous state by stirring. (iii) The distinction between the two cases, stirred or unstirred, is unimportant, after all. A measurement of the enthalpy of mixing as a function of composition and temperature allows one case to be calculated from knowing the other. (iv) Our method measures the temperature increase of one region of the sample only and the sample is assumed to be at this temperature throughout. Because of the sample geometry this assumption should hold in the homogeneous region. But, since the two layers are expected to have different thermal conductivities, equilibrium will not be established equally in the two layers. Also, the sampling point could shift from one phase to the other as the meniscus between them moves past the sampling point.² For these reasons we did not attempt to measure the specific heat below the critical temperature.

The specific heat was measured with a pulse technique, the differential-thermocouple output being recorded with a Moseley 7000AR recorder and the calorimeter temperature measured with a Leeds and Northrup K-5 potentiometer. The temperature increases of the sample were determined graphically by extrapolating pre- and postpulse drifts to the midpoint of the heating pulse (typically 40 sec long at a rate of 20/h) and, away from T_c , were typically 60 m°C. This was kept so small since its size limits the closest approach to T_c possible. While no attempt was made to accurately determine the absolute temperature or value of T_c , the quantity $(T - T_c)/T_c$ was measured with a resolution of 10^{-5} . During the heating pulse no increase

in shield temperature was detected, and changes in input power or length of pulses by factors from 0.2 to 5 did not change the specific heat measured within the accuracy of the measurement.

The current to the heater was switched electronically and the energy input per pulse was calculated by $E = tI^2R$, where t is the length of the pulse, R is the heater resistance of 11.5 Ω, and I is the current which was monitored as it passed through a 0.1-Ω shunt. A typical heat pulse was (40 sec) $(0.0454 \text{ A})^2 \times (11.5 \text{ Ω}) = 0.923 \text{ J}$; thus, away from the critical temperature the specific heat of the whole sample was $c_p = 15.4 \text{ J K}^{-1}$. Using the values¹⁶

$$c_p(\text{Hg}, 200^\circ\text{C}) = 27.13 \text{ J mole}^{-1} \text{ K}^{-1},$$

$$c_p(\text{Ga}, 200^\circ\text{C}) = 27.8 \text{ J mole}^{-1} \text{ K}^{-1},$$

$$c_p(\text{Pyrex}, 200^\circ\text{C}) = 1.0 \text{ J g}^{-1} \text{ K}^{-1},$$

the specific heat of our sample plus container, neglecting the thermocouple and the heater, adds up to 15.18 J K⁻¹. In view of the fact that the heater was wound over the length of the Pyrex tube filled with liquid metal only, the agreement between the two values is probably fortuitous. An independent measurement of the specific heat of the empty Pyrex tube would not give better accuracy since the dynamic thermal behavior of the empty glass tube would be considerably different, due to the order-of-magnitude difference in thermal conductivities between Pyrex and the liquid metals. The contributions of the glass cell and the background specific heat of the Ga-Hg mixture were, however, considered to be known insufficiently accurately in order to subtract them out; therefore, in what follows, the data are presented for the total measured specific heat, i. e., for the Ga-Hg sample plus the Pyrex cell. Since our measurements are limited to the region above T_c we drop the superscript of the parameters of Eq. (1). The accuracy of our experimental values is estimated to be about 5%. For better over-all accuracy in the absolute values of the excess specific heat a metallic sample container should be used, e. g., a tantalum or molybdenum crucible.

IV. RESULTS AND DISCUSSION

Figure 1 shows the total measured specific heat c_p vs temperature and Table I lists data near T_c . Each point plotted is an average of at least two measurements; the data of two runs are displayed. The inset of Fig. 1 shows the peak with an expanded temperature scale. The intersection of the two smooth lines fixes T_c within the uncertainty indicated by the error bar. The T_c thus determined, 201.791°C, agrees well with previously published values^{1,2,7}; it has to be kept in mind that the pressure inside the sample cell is unknown and T_c is probably lower than it would be at atmos-

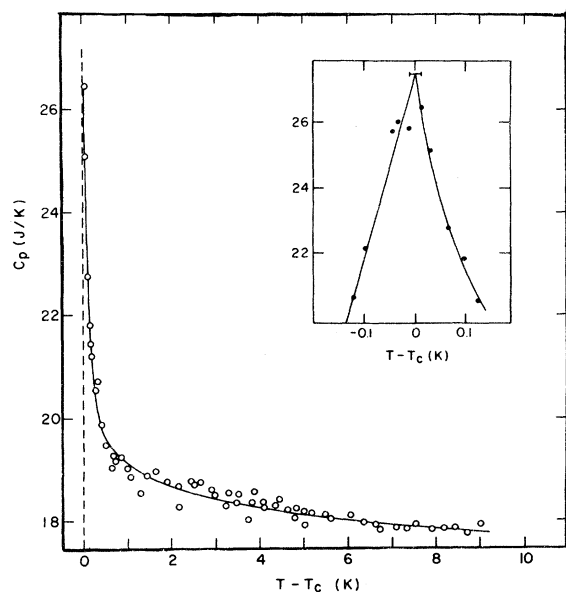


FIG. 1. Plot of the total specific heat above the critical temperature of a mixture of 49.74-at.% Hg in Ga. Inset: the critical region plotted with an expanded temperature scale.

pheric pressure. Standard thermocouple tables were used in converting the millivolt readings to temperature. A plot of c_p vs $\log_{10}(T - T_c)$ is shown in Fig. 2, where two least-squares fits to Eq. (1) are also drawn with $\alpha = 0.1$ and 0.5 , respectively. The error bars for the points close to T_c span the same interval as the error bar in the inset of Fig. 1. Table II lists the parameters of Eq. (1) found by least-squares analysis, given α and T_c . The fits with $\alpha = 0.3$ and 0.4 , respectively, give the

TABLE I. Specific heat of sample and container.

T (°C)	c_p (J/K)	T (°C)	c_p (J/K)
201.798	26.465	203.195	18.865
201.819	25.084	203.371	18.961
201.860	22.779	203.780	18.716
201.896	21.786	204.034	18.845
201.927	21.442	204.181	18.723
201.957	21.130	204.257	18.680
201.963	21.204	204.655	18.584
202.035	20.878	204.906	18.499
202.051	20.548	205.203	18.295
202.143	19.862	205.264	18.472
202.241	19.547	205.789	18.314
202.262	19.464	206.327	18.160
202.351	19.475	206.707	17.858
202.421	19.231	207.326	18.012
202.455	19.265	208.468	17.775
202.633	19.334	210.143	17.819
202.842	18.836		

TABLE II. Results of least-squares fits to Eq. (1) for given α and T_c .

α	c_p^0 (J/K)	c/α (J/K)	rms deviation
0.1	9.45	22.62	0.401
0.2	14.54	24.53	0.288
0.3	16.26	34.29	0.207
0.4	17.15	52.06	0.211
0.5	17.70	81.50	0.295

smallest rms deviations. On the other hand, the values of c_p^0 determined by the fits with $\alpha = 0.2$ and 0.3 agree best with our estimate of the specific heat of the empty glass cell and the liquid metals in the absence of a singularity. The largest value measured of the anomalous contribution is about 2.65 times the background contributions of the metals. Our conclusion is that the specific heat has a singularity near the critical temperature that goes as $(c_p - c_p^0) \approx \epsilon^{-\alpha}$, where $\alpha = 0.3 \pm 0.1$ in the reduced temperature interval $5 \times 10^{-5} < \epsilon < 2 \times 10^{-2}$.

Thus the singularity in the specific heat of this critical mixture of liquid metals is stronger than logarithmic; our value of α is certainly not incompatible with values measured in other critical systems.¹⁷ Together with the value of $\beta = 0.335$

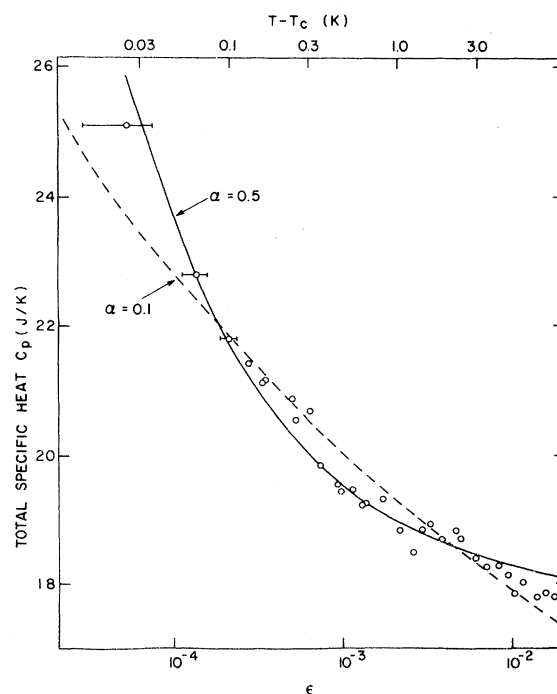


FIG. 2. Total specific heat vs $\log_{10}(T - T_c)$. Error bars reflect the uncertainty in T_c indicated by the error bar in inset of Fig. 1. The solid lines labeled $\alpha = 0.5$ and $\alpha = 0.1$ are least-squares fits to Eq. (1).

$\pm 0.005^1$ the present determination of $\alpha = 0.3 \pm 0.1$ leads, with the Griffiths-Rushbrook inequalities (written as equalities),¹¹ to the values $\gamma = 1.03 \pm 0.11$ and $\delta = 4.07 \pm 0.37$, respectively. Egelstaff and Ring¹¹ deduce a value of $\delta \approx 4$ from the data of Predel⁷ on this system. From the present data it

follows that metallic binary mixtures do not show considerably different behavior in the critical region from the nonconducting binaries, and the earlier contention of Egelstaff and Ring¹¹ that the interatomic forces affect the values of the critical exponents does not seem to hold in this instance.

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¹H. K. Schürmann and R. D. Parks, *Phys. Rev. Letters* **26**, 357 (1971).

²See also P. D. Adams, *Phys. Rev. Letters* **25**, 1012 (1970); H. K. Schürmann and R. D. Parks, *ibid.* **26**, 835 (1971).

³M. E. Fisher and J. S. Langer, *Phys. Rev. Letters* **20**, 665 (1968).

⁴F. C. Zumsteg and R. D. Parks, *Phys. Rev. Letters* **24**, 520 (1970).

⁵K. N. Lee, R. Bachmann, T. H. Geballe, and T. P. Maita, *Phys. Rev. B* **2**, 4580 (1970).

⁶D. S. Simons and M. B. Salamon, *Phys. Rev. Letters* **26**, 750 (1971).

⁷The method of differential thermal analysis, which consists of locating singularities in the cooling rate (hence, specific-heat anomalies), has been used in various instances to determine the coexistence curve in binary liquid metals. However, in these studies the specific-heat anomalies were not studied in any detail. For the Ga-Hg system, see B. Predel, *Z. Physik. Chem. (Frankfurt)* **24**, 206 (1960).

⁸H. K. Schürmann and R. D. Parks, *Phys. Rev. Letters* **27**, 1790 (1971). In the first paragraph on p. 1793 containing the results in the Ga-Bi system it should read: "Below T_c the two layers formed exhibit resistive behavior

which is qualitatively the same as that observed (by us) in the Ga-Hg system [*Phys. Rev. Letters* **26**, 357 (1971); **26**, 835 (1971)]. Above T_c the behavior of the uniform mixture was analogous to that observed in the Li-Na system, e.g., dp/dT increases as $T \rightarrow T_c$ from above, in contradistinction to Adams's results."

⁹H. Schmidt, G. Jura, and J. H. Hildebrand, *J. Phys. Chem.* **63**, 297 (1959).

¹⁰M. Fixman, *J. Chem. Phys.* **36**, 1961 (1962).

¹¹P. A. Egelstaff and T. W. Ring, in *Physics of Simple Liquids*, edited by H. N. V. Temperley (North-Holland, Amsterdam, 1968), Chap. 7.

¹²V. P. Skripov and V. M. Kostin, *Russ. J. Phys. Chem.* **34**, 718 (1960).

¹³Yu. P. Blagoi and V. G. Gusak, *Zh. Eksperim. i Teor. Fiz.* **56**, 592 (1969) [*Sov. Phys. JETP* **29**, 326 (1969)].

¹⁴J. P. Brouwer, A. M. Vossepoel, C. J. N. Van Den Meijdenberg, and J. J. M. Beenakker, *Physica* **50**, 125 (1970).

¹⁵T. Alvesalo, P. Berglund, S. Islander, G. R. Pickett, and W. Zimmermann, Jr., *Phys. Rev. Letters* **22**, 1281 (1969).

¹⁶Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer, Berlin, 1967), 6th ed., Vol. IV, p. 916; and Vol. II, p. 482.

¹⁷P. Heller, *Rept. Progr. Phys.* **30**, 731 (1967).

Electron Momentum Distribution in Vanadium*

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The Compton profile of polycrystalline vanadium has been measured using 59.54-keV γ rays from an ^{241}Am source. In the regions of medium and high electron momentum, the observed profile coincides with that calculated from Hartree-Fock free-atom wave functions for the outer-electron configuration $3d^4 4s$. At small momentum values the experimental results deviate significantly from those predicted by Hartree-Fock theory.

I. INTRODUCTION

The importance of momentum distributions has long been recognized in x-ray Compton scattering from electronic systems.¹ Only very recently, however, have the measurements been productive. A wide range of systems has been studied at $\text{MoK}\alpha$ or $\text{AgK}\alpha$, including inert gases,² diatomic^{2,3} and polyatomic⁴⁻⁷ molecules, and light crystalline elements and compounds.⁸ All these experiments have

yielded decisive information about the electron momentum distributions.

Another possibility for studying the electron momentum density is the Compton scattering of γ rays. A suitable radioactive source is, for example, ^{241}Am , which emits 59.54-keV photons. The use of ^{241}Am γ rays and a solid-state detector in conjunction with a multichannel analyzer instead of $\text{MoK}\alpha_1\alpha_2$ (17 keV) or $\text{AgK}\alpha_1\alpha_2$ (22 keV) x rays and a crystal spectrometer offers some advantages.