Observation of a Metastability Limit in Liquid Gallium

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We report neutron-scattering measurements on highly supercooled liquid gallium droplets showing a vanishing quasi-elastic frequency width as the temperature is reduced. The width tends towards zero at a temperature within 1 standard deviation of the value $T_L = 150 \pm 1$ K at which gallium is always observed to become crystalline. This suggests the interpretation of T_L as a metastability limit, below which the liquid state becomes unstable with respect to infinitesimal fluctuations.

By dividing gallium into small droplets,[1] it is possible to supercool the liquid to around half its normal melting temperature of 303 K. This offers the experimenter a unique opportunity to investigate the ultimate stability of the liquid state as the temperature is reduced. For many years there have been theoretical discussions[2] of a stability limit, where a supercooled liquid would become unstable with respect to infinitesimal fluctuations rather than the finite stimulus needed to nucleate a supercooled liquid. However a feature of most theories is that the limit is associated with a divergence in the structure factor $S(Q)$. X-ray measurements of $S(Q)$ made on supercooled gallium droplets,[3,4] in fact, show $S(Q)$ to be only weakly temperature dependent close to 150 K where freezing has always been observed to occur.[5] X rays also show that when freezing occurs from temperatures near 150 K, it is always to the crystalline β phase[6] although gallium has several other solid phases which may be formed if crystallization takes place at higher temperatures.

Amorphous gallium has been prepared by vapor deposition onto helium-cooled substrates,[7] but is observed to be unstable on heating beyond 15 K, transforming again to the crystalline β phase. The structure factor from the amorphous gallium measured by x rays at 5 and 13 K is similar in form to that expected from extrapolation of the temperature dependence of $S(Q)$ in the supercooled liquid. A glass transition within the liquid phase gives anomalies in the viscosity and specific heat. Calorimetric measurements in the range 300 to 190 K and differential-thermal-analysis measurements on single droplets down to 150 K have been performed and show no sign of any glass transition.[8] Thus there is strong evidence that liquid gallium is only metastable above 150 K, but the static measurements described so far show no effects anticipating the transition.

Such effects can be shown by inelastic neutron scattering which reveals the time dependence of the density fluctuations. The cross section observed with a momentum transfer $\hbar Q$ and energy transfer $\hbar\omega$ gives $S(Q,\omega)$, the Van Hove scattering function.[9] Several experiments measuring $S(Q,\omega)$ in bulk liquid gallium in the temperature range above 270 K have already been performed.[10-14] They agree in showing quasi-elastic frequency distributions which are approximately Lorentzian in form with a minimum width at wave vector $Q_0 = 2.5$ Å corresponding to the peak in $S(Q)$ and which decrease with temperature much more rapidly than the $T^{1/2}$ variation expected from the expression for the rms width.[15] The present work extends these studies to close to the crystallization temperature of 150 K.

The emulsions were prepared by using an ultrasonic generator to form droplets of mean size 5 μm under ethyl alcohol. The samples were washed with deuterated methyl alcohol, most of which could then be decanted and evaporated off so that the samples contained a negligible proportion of alcohol. Figure 1 shows the similar form of the frequency distributions observed from the dispersed emulsions (closed circles) compared with bulk gallium (open circles). The samples were contained in rectangular plate cells of thickness 3 mm with 0.1-mm vanadium sheet windows. Samples $P3$ and $P4$ were successfully cooled to 213 K without the formation of any solid detectable from Bragg scattering so that frequency distributions at many values of Q were taken

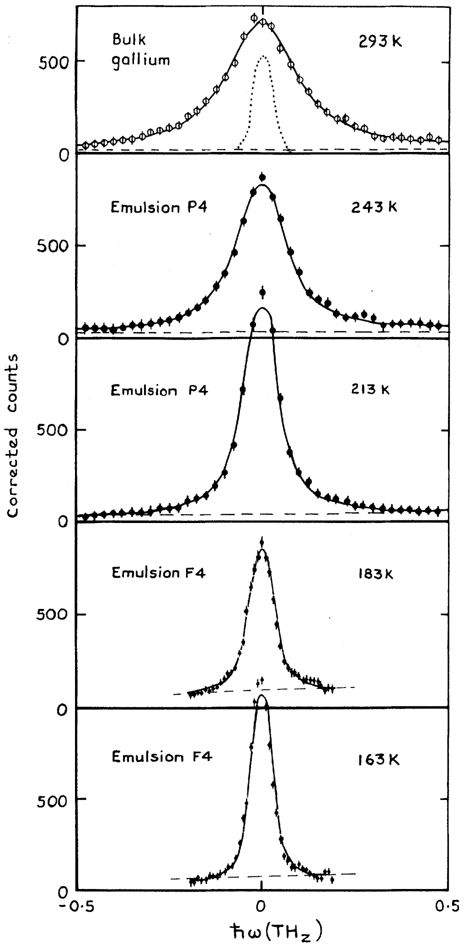

FIG. 1. Constant-Q scans at $Q_0 = 2.50$ Å^{-1} (corresponding to the peak in the structure factor) in bulk and dispersed liquid gallium. The solid lines represent the best-fit Lorentzians, convoluted with the experimental resolution function (shown dotted). The fitted background is shown dashed.

at this temperature. A further sample $F4$ was cooled to 163 K with only a small fraction of droplets crystallized into the β phase. This did not prevent the measurement of frequency distributions at $Q_0 = 2.5$ Å since no β-phase powder peaks occur in this region, but measurements near the shoulder in $S(Q)$ at $Q_{00} = 3.12$ Å^{-1} were not possible.

Our experiments were performed on the triple-axis spectrometer IN3 at the Institute Laue-Langevin at Grenoble.[16] Neutrons of wavelength 1.90 Å were monochromatized by a copper (220) reflection and analyzed by a germanium (333) reflection. The resulting high scattering angles enabled an energy resolution of 0.05 THz (full width at half-height) to be achieved with collimations defined only by the incident neutron guide (0.2°), a 12-mm aperture on the sample, and the 10-mm diam of each of a bank of eleven adjacent ^{3}He counters. Employing these counters in a MARX mode[17] enabled improved statistics to be obtained without degrading the energy resolution, but at the expense of degrading the Q resolution from 0.01 to 0.04 Å^{-1}.

The frequency distributions measured at the peak in $S(Q)$ at 2.5 Å^{-1} and showing the general reduction in the quasi-elastic frequency width as the temperature is reduced are given in Fig. 1. Measurements have been corrected for the container and background scattering and multiplied by the appropriate factors to make them proportional to $S(Q,\omega)$.[9] No correction has been made for multiple scattering since we do not have the required full information on $S(Q,\omega)$. However its effect is certainly to make the frequency distributions broader rather than narrower. We also neglect the 13% contribution from incoherent scattering in gallium ($\sigma_{\rm coh} = 6.5$ b, $\sigma_{\rm inc} = 1.0$ b). From the few cases where the coherent and incoherent scattering functions have been independently measured by isotope separation[18] it would appear that in the high-Q region of the present experiment the Vineyard approximation[19] holds: That is, the two frequency distributions are similar and scale roughly as their peak height at a given Q. Thus we expect that at low temperatures when the coherent contribution is large, the effect of the incoherent contribution will be even smaller than at higher temperatures. As a check on our measured frequency distributions we evaluated their zeroth moment (integrated intensity) at 213 K, which followed within 20% the variation of $S(Q)$. The second-moment relationship[15] is not possible to check because the observed widths have little relevance to the rms widths because of the divergent second moments of Lorentzian distributions. The solid lines in Fig. 1 are the best-fit Lorentzian frequency distributions convoluted with the the resolution function (an example of which is shown dotted in the upper scan). The dashed line represents the fitted background. The corresponding widths (full width at half-height) shown by the solid circles in Fig. 2 together with the earlier results,[10,12,13] suggest a linear increase in the width W with a gradient $dW/dT = 0.0016 \pm 0.0002$ THz K^{-1} and an intercept $T_L = 157 \pm 10$ K. The widths measured at $Q_{00} = 3.12$ Å on the shoulder of $S(Q)$ are appreciably larger at 213 K but have a steeper temperature dependence of order 0.0024 THz K^{-1} and are consistent with the same

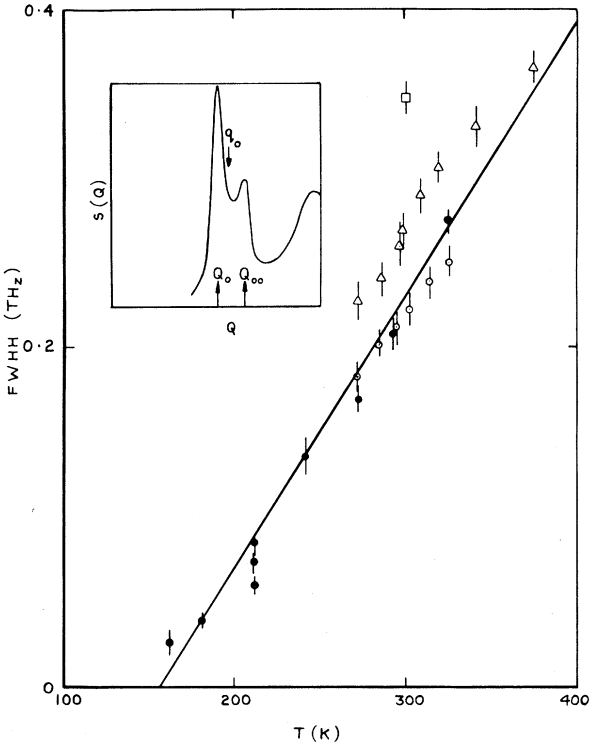

FIG. 2. The fitted Lorentzian full widths at half-height for scans at $Q_0 = 2.50$ Å^{-1} (filled circles). Previous measurements are shown by open symbols and are from Refs. 13 (circles), 10 (triangles), and 12 (squares). The line represents a fit to all the data shown, but giving reduced weights to results from Refs. 10 and 12 which are not consistent, within their quoted errors, with those from Ref. 13 and the present work. Measurements were taken at the wave vectors Q_0 and Q_{00} whose positions on the measured structure factor at 163 K are shown on the inset (from Ref. 3). The zero in the calculated pseudopotential, indicated by q_0, is also shown.

value of T_L. This value of T_L coincides, within experimental error, with the observed minimum crystallization temperature of gallium droplets. We therefore interpret T_L as the metastability limit of the liquid state. Since the frequency distribution width vanishes as the limit is approached while its area, proportional to $S(Q)$, remains slowly varying it follows that an associated divergence occurs in the elastic scattering function $S(Q_0, \omega = 0)$. This may be written in terms of the time average of the intermediate density correlation function $\langle S(Q_0, t)\rangle$, which thus diverges while its instantaneous value $S(Q_0, t = 0)$, related to $S(Q_0)$, remains finite.

While we have as yet no satisfactory theory for the metastability limit, it seems probable that its occurrence in gallium stems from its electronic structure. Heine and his collaborators[20] have argued that gallium's complicated crystal structures and relatively low melting temperature are caused by the proximity of the first zero in its pseudopotential (q_0) to its lattice periodicity in a close-packed structure. It is then energetically favorable for the reciprocal-lattice vectors of the solid phase to avoid q_0 by forming complex structures, and similarly in the liquid to remove weight in the structure factor at q_0 by forming the observed double-peaked structure factor having a minimum near q_0. Badiali and Regnaut[21] have recently analyzed the temperature dependence of $S(Q)$ from the point of view of an underlying hard-sphere structure modulated by the pseudopotential effects. The extension of the pseudopotential methods to a dynamic model of the liquid may well be a prerequisite to any satisfactory explanation of our observations.

We conclude that, as the metastability limit is approached from above, there is an approximately logarithmic divergence of the time-averaged fluctuation density $S(Q_0, \omega = 0)$ reminiscent of the approach to a second-order phase transition. However the incipient ordered state in the liquid is unstable with respect to infinitesimal fluctuations and a first-order transition results forming the only thermodynamically stable state, the crystalline solid.

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Magnetic Interactions in Dilute *Ag*Mn Alloys

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Measurements are presented of the magnetization M up to 50 kG between 1.8 and 4.2 K and the susceptibility χ from 1.8 to 100 K of three dilute *Ag*Mn alloys of nominal concentrations 630, 1000, and 1370 ppm Mn. Both M and χ follow scaling laws well. The strength V_0 of the Ruderman-Kittel-Kasuya-Yosida interaction between two Mn impurities has been determined from expressions for the high-field behavior of M in the presence of such interaction, yielded by a virial expansion of the free energy. The value for V_0 is $(2.4 \pm 0.4) \times 10^{-25}$ eV cm^3. The effective $|J|$ value estimated from V_0 is 0.7 ± 0.1 eV.

Recently interest in alloy research has been shifting from the extremely dilute region ($T_I < T_K$, where T_I is the measure of average interactions between solute atoms and T_K is the Kondo temperature) in which the single-impurity Kondo effect dominates to the more concentrated region in which the interactions between impurities can no longer be neglected. The strength V_0 of the Ruderman-Kittel-Kasuya-Yosida[1] (RKKY) interaction, $V(r) = V_0 \cos(2k_F r)/r^3$ (for $k_F r \gg \pi$), between two Mn impurities and the effective $|J|$ value in *Ag*Mn alloys have been determined by magnetization measurements at high fields and are presented here. The *Ag*Mn alloy system was chosen because T_K is very small, so that in the dilute limit the solute has a good magnetic moment down to very low temperatures; and because the electronic structure of Ag is simple it can be safely approximated by a free-electron model. It is thus unlike *Au*Fe, for example, where the effect of T_K on the interaction behavior is clear in the results of Laborde and Radhakrishna.[2]

Three *Ag*Mn alloys with respective nominal concentrations of 630, 1000, and 1370 ppm Mn were examined. The starting materials were 99.9999% Specpure Ag (Johnson Matthey) and 99.99%-pure Mn from Koch-Light Labs Ltd. The samples were made by diluting a 5.43-at.% *Ag*Mn master alloy in an arc furnace filled with $\frac{2}{3}$ atm argon, and forming short cylinders of about 3 mm diameter. All samples were cleaned by a mixture of NH_4OH and H_2O_2. Measurements were carried out by a force (Faraday) method using a superconducting solenoid (0–50 kG) with separate super conducting gradient field coils; the forces were measured with a Beckman LM-600 microbalance.