

Temperature Dependence of the Dynamic Structure Factor for Supercooled $\text{Sn}_{1-x}\text{Pb}_x$ Alloys: A Test of Instability Theories for the Liquid-Solid Phase Transition

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Measurements of the dynamic structure factor at Q_0 , the momentum transfer of the first maximum of $S(Q, 0)$, have been made for droplet samples of Sn and Sn + Pb liquid alloys into the supercooled region. It is shown that half-width variations with temperature are inconsistent with expectations from instability theories for the liquid-solid phase transition, but correlate well with changes in atomic diffusivities with alloy composition.

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Several authors¹⁻³ in recent years have advanced theoretical reasons for believing that the limit on supercooling of simple liquids may be set by an instability ("soft diffusive mode") which is expected to develop at nonzero Q vector, specifically, at Q_0 , the first maximum in the liquid structure factor. An expected divergence in $S(Q)$ at the instability has been sought in experiments by Carlson, Feder, and Segmüller⁴ and Gläser and co-workers⁵ without encouraging results, though an expected narrowing of $S(Q, \omega)$ was observed in its initial stages for several liquid metals in the latter study.

In 1975 a striking experimental result for $S(Q, \omega)$ was reported by Bosio and Windsor.⁶ They succeeded in measuring the dynamic structure factor of supercooled liquid gallium droplets down to 163 K ($T_m = 303$ K). Their findings, combined with those of Gläser *et al.*,⁵ established a linear decrease of the linewidth from 1253 to 150 K, which goes far beyond the region of validity of the instability theory. However, their results did seem to establish some connection between the homogeneous nucleation phenomenon and fluctuations at Q_0 , since they found that the lifetime of fluctuations of this wave vector measured by the half-width of the dynamic structure factor $S(Q = Q_0, \omega)$ tended to infinity at the same temperature as nucleation was observed. Such behavior would imply that the liquid has a special, indeed irresistible, opportunity to nucleate crystals at that temperature since Q_0^{-1} is the crystal lattice

spacing. Although it was not specifically discussed by the authors, it could be argued that other, especially low- Q , fluctuations would have shorter lifetimes, and hence nucleation could occur while the liquid was still in a highly fluid condition, as is known to occur in practice.

It is known that $S(Q, \omega)$ will also be affected by the decrease in diffusivity with decreasing temperature.⁷ As we will show later, this effect will also cause $S(Q, \omega)$ half-widths to tend to vanish at finite T . Accordingly, we have designed an experiment to test the *qualitative* rather than the quantitative predictions of instability theories. Specifically, we have chosen to study the variation of $S(Q = Q_0, \omega)$ in some *binary* mixtures of metals where the diffusivity variation with composition predicts a particular form of composition dependence for the temperature at which the width of $S(Q = Q_0, \omega)$ tends to zero, while the known variation with composition of the homogeneous nucleation temperature predicts the opposite form of dependence.

The Sn-Pb system is a favorable case for study since the nucleation temperatures for emulsion samples are known,⁸ and the diffusivity variations with temperature can be assessed from accurate viscosity data available in the literature.⁹

Droplet samples were produced by mechanical shearing of liquid Sn, or Sn plus 10, 20, and 30 wt.% Pb, in hot organic fluids containing oxidizing additives.⁸ Greatest supercooling ($\sim 150^\circ\text{C}$) in

these samples is obtained when the oil remains in contact with the droplets, but this is not permissible for neutron scattering studies because of the powerful scattering by protons in the organics. Shortly before loading, all traces of oil were removed by repeated washing in acetone. (In the first case studied, 10 wt.% Pb, a residual film of oil ruined the experiments.) It now appears that the use of an inert atmosphere to prevent a change in oxidation state of the surface coating might yield deeper supercooling of powders to temperatures observed in preliminary differential scanning calorimetry DSC studies of these alloys, but this was not invoked in the present series.

For the scattering experiment, the dry powder was placed in a thin Al cylindrical container, and separated into ten sections by Al-Gd absorbing disks to minimize multiple scattering. Uniform temperatures were obtained by appropriate heater-coil and heat-shield arrangements. Sample temperature was controlled during the 24-h runs to 0.1°C and measured to 1°C by Cr-Al thermocouples placed at the sample edge. Details are given elsewhere.¹⁰

The experiment was performed with use of the cold-neutron triple-axis spectrometer IN12 at the high-flux reactor of the Institut Laue-Langevin in Grenoble. The spectrometer was run with constant incident neutron wave vector $k_i = 1.5 \text{ \AA}^{-1}$, and energy changes were made between -0.3 and $+0.3$ THz in steps of 0.02 THz at $Q = 2.235 \text{ \AA}^{-1}$. Determinations of $S(Q, 0)$ near the first maximum were made for each sample, as well as the necessary empty can, empty furnace, and instrument resolution function runs (details are given elsewhere). The resolution function is a Gaussian of full width at half maximum (FWHM) of 0.034 ± 0.001 THz.

The sample measurements were split into several repeated runs, each of 3000 sec, so that runs during which nucleation set in could be discarded (this happened only twice during the whole experiment). The repetitive-run procedure would also have avoided any distortion of the Lorentzian form due to a small degree of crystallization, if this had proceeded continuously during the run. Some crystals can be tolerated because they scatter only in the ω range of the resolution function. Details of the temperature sequences necessary to maximize the temperature ranges of the study are given elsewhere.¹⁰

All of the short (3000-sec) scans of the same run were summed and then corrected for back-

ground and empty-container intensities (see Fig. 1). Neither absorption nor multiple scattering effects change the widths measurably, and hence corrections are unnecessary. The corrected data were multiplied by $k_f^3 \cot\theta_A$ (θ_A is the analyzer angle) and fitted by a Lorentzian (convoluted with the Gaussian resolution function of the spectrometer) after discarding the three data points at $\nu = -0.02, 0,$ and $+0.2$ THz which contain contributions from crystallized droplets and droplet-coating material. In one case where the sample was largely crystallized, a Gaussian plus a Lorentzian (likewise convoluted with the resolution function) was also used. The case of liquid tin at 570 K is used in Fig. 1 to illustrate the

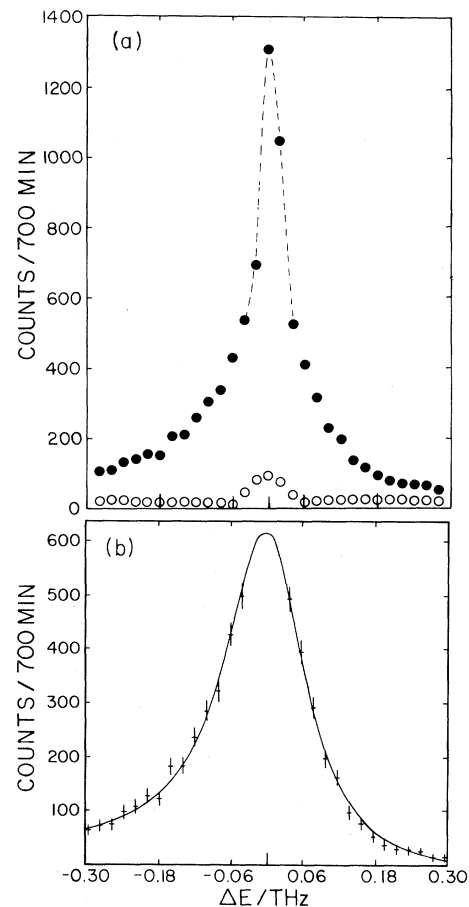


FIG. 1. (a) Neutron scattering intensity vs energy change for liquid tin at 570 K, at $q = 2.235 \text{ \AA}^{-1}$ (solid points) and of the background normalized to the sample runs (open circles). The Gaussian part at $\omega = -0.2$ to 0.2 THz is due to scattering from residual solid material, presumably droplet-coating oxides. (b) Lorentzian fit to the background-corrected intensity data, after discarding the three central points.

data reduction. Results for the FWHM, after final deconvolution of the measured spectrometer resolution function, are given in Fig. 2.

Figure 2 shows that for each composition studied the FWHM varies linearly with T and, as found for Ga,⁶ tend to vanish at a temperature in the vicinity of the lowest observed droplet nucleation temperature. All points lie within statistical uncertainty of the drawn lines except for pure Sn at 425 K. In this case the sample was largely crystallized: The appropriate Gaussian plus Lorentzian analysis gave a FWHM for the Lorentzian component which falls on the line of Fig. 2 (point marked G+L).

The temperatures, designated $T_0(S(Q_0, \omega))$, at which the lines extrapolate linearly to zero FWHM, are all within 50 K of the lowest recorded nucleation temperatures for emulsion droplet

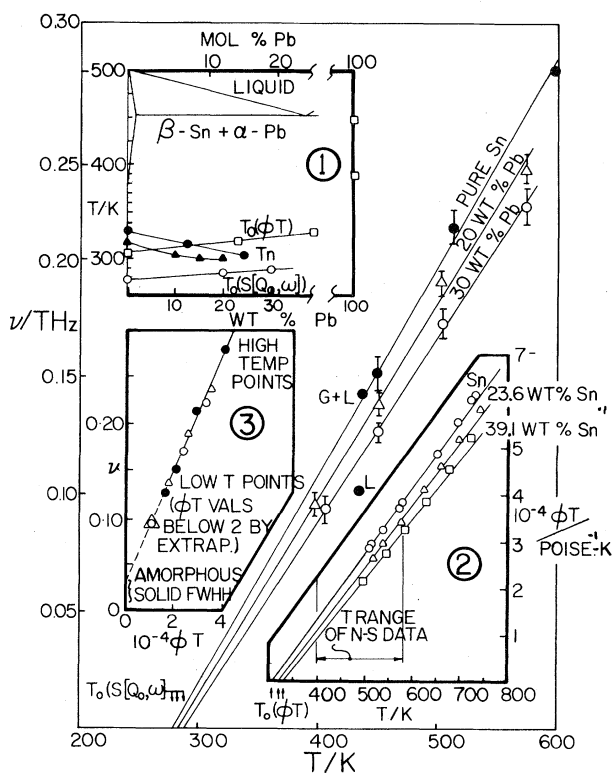


FIG. 2. Half-width of $S(Q_0, \omega)$ vs temperature for pure Sn and two Sn + Pb alloys, showing extrapolated points of vanishing half-width, $T_0(S(Q_0, \omega))$. Inset (1): Comparison of vanishing half-width and vanishing diffusivity temperatures, with observed nucleation temperatures, T_n . Inset (2): Fluidity-temperature product vs T showing extrapolated points of vanishing ϕT ($\propto D$), $T_0(\phi T)$, for pure Sn, pure Pb, and two Sn + Pb alloys. Inset (3): Direct correlation of diffusivity (as ϕT) with FWHM of $S(Q_0, \omega)$.

samples (of which two independent data sets that use different droplet-coating techniques⁸ are shown), and so at first sight our measurements might seem to support the interpretation given by Bosio and Windsor.⁶ In fact, if measurements had been confined to pure Sn and allowance were made for the fact that Sn is more difficult to protect against surface nucleation than Ga (which would imply that for Sn the true T_n is somewhat lower than the lowest emulsion T_n value, 322 K, yet recorded⁸), it might be concluded that tin also crystallizes via a $Q = Q_0$ kinetic mode-instability mechanism. However, both the extrapolated $T_0(S(Q_0, \omega))$ points and the experimental T_n values (for a given coating technique) are determined to greater precision than the differences between them, and the outstanding result, summarized in inset (1) in Fig. 2, is that they change in *opposite* directions with increasing lead content. (T_n , as always, scales with the liquidus temperature.) This result suggests that either we have been monitoring the wrong Q value or some other factor, less interesting than an impending phase change, exerts the primary influence on the $S(Q_0, \omega)$ temperature dependence. We next offer evidence that, as Sjölander and Turski have suggested,¹¹ the latter is the correct alternative.

Line narrowing can be expected from the general slowing down of the diffusion process through which nonpropagating density fluctuations at any Q vector of order Q_0 or smaller must decay, in addition to any special features associated with the component of $Q = Q_0$. It therefore makes sense to calculate how the line narrowing due to a general diffusive slowing down should behave with composition. Since alloy diffusivity data are not available we use the fluidity-temperature product ϕT , which should scale with D according to the Stokes-Einstein equation

$$D = (k_B/6\pi\eta r)T\phi \quad (1)$$

(r is the particle radius). The equation applies well to simple liquids in the fluidity range of this study, and even describes the behavior of more complex and viscous fluids over wide density and T ranges with ~ 4 replacing 6 in the denominator.¹²

Accordingly, we plot ϕT vs T in Fig. 2, inset (2), for three compositions spanning the range of our study, and extrapolate to $\phi T = 0$ to compare qualitatively the composition dependence of these intercept temperatures (vanishing diffusivity temperatures), $T_0(\phi T)$, with those from the line-narrowing study. The fluidity data used are

taken from the precise work of Kanda and Colborn.⁹ φT is not strictly linear in T (viscosity follows Arrhenius behavior⁹) so that, for consistency, we base the extrapolation on linear best fits to the φT data in the T range of the neutron-scattering study. Figure 2, inset (2), shows a qualitative agreement between the composition dependences of the FWHM and φT intercepts which is absent in the comparison with T_n .

The correlation of FWHM with diffusivity can be shown more directly and forcefully by plotting the individual FWHM values against the φT product at the same temperature [the latter by interpolation of the data shown in Fig. 2, inset (2)]. This plot [see Fig. 2, inset (3)], collapses the data for different compositions onto a single straight line which has a positive FWHM intercept. The latter is consistent with the knowledge that $S(Q, 0)$ remains broader in glasses ($D=0$) than in crystals.

In summary, the FWHM data fail to support instability-theory expectations but correlate strikingly with simple diffusivity predictions for this system. To the extent that these transport coefficients conform to Arrhenius behavior at small D ,⁹ we should stress that there is no significance in the linear φT extrapolation shown in Fig. 2, inset (2). Below 350 K, corresponding to FWHM values of ~ 0.05 THz, the plots of FWHM, φT , or D should begin to curve strongly to lower temperatures. Indeed, the best fit to the FWHM values plotted by Bosio and Windsor for Ga (which go to low FWHM values)⁶ shows just this form. Finally, the connection of the narrowing of $S(Q, \omega)$ with the diffusivity which we propose helps explain why the linewidths found by Bosio and Windsor⁶ in the supercooled state and those found by Gläser *et al.*⁵ at high temperatures fall on the same straight line over an interval of tempera-

ture as large as 1100 K.

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