Superheating and Supercooling of Lead Precipitates in Aluminum

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Thermal hysteresis is observed in x-ray-diffraction studies of the melting and solidification of small crystalline precipitates of lead in aluminum. Reproducible superheating as well as supercooling is present in successive heating sequences demonstrating that they are intrinsic physical phenomena. For lead precipitates of mean size 140 and 270 Å, the width of the hysteresis loop is 88 and 62 K, respectively. These results are discussed in a phenomenological context considering the lack of free surfaces.

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The melting of crystalline matter is one of the most fundamental order-disorder transitions in nature. Yet, because of the abruptness and destructive nature of melting, what has been revealed about this intriguing transformation is still today sparse. Insoluble epitaxially aligned precipitates offer a unique model system in which the melting transformation can be studied cyclically, e.g., nondestructively. This is because the epitaxial alignment between the precipitates and the host matrix leads to an effective orienting field. We report on the study of small Pb crystals realized as precipitates in an aluminum single crystal. Superheating as well as supercooling of the lead precipitates are observed in a hysteresis loop between melting and solidification.

The effort to find and test a phenomenological description of melting has included the consideration of several different mechanisms for bulk melting: dislocation initiated,[1] grain-boundary initiated,[2] entrophic,[3] and surface initiated.[4] For glass-forming materials the kinetics of melting of the crystalline phase is particularly slow; for quartz, superheating up to 450 K can be maintained for a few minutes.[5] Metallic crystals generally do not superheat because the free surface acts as a potent heterogeneous nucleation site for the melt.[6] Computer simulations of slabs of atoms interacting with Lennard-Jones potentials suggested that melting may be surface initiated.[7,8] A study of rods of perfect crystals of tin[9] showed that the melting nucleated at the surface. Rutherford backscattering studies of lead showed premelting of the (110) surface.[10,11] Small particles of gold melt at a reduced temperature;[12] for example, a gold particle 150 Å in diameter melts 60 K below the bulk melting point. Indium particles in aluminum[13] showed thermal hysteresis and melted at temperatures up to 37 K above the bulk melting point; however, the pressure in the indium was unknown. Melting of thin (10–100 Å) polycrystalline lead films sandwiched between thin germanium layers[14] and of lead aggregates in SiO also exhibited thermal hysteresis,[15] and the melting point was reduced relative to the bulk. In a study of the kinetics of melting of lead crystallites on a carbon surface[16] superheating up to 2 K was observed, depending on size and shape. Recently, a phenomenological theory for very small clusters hint at a broadening of the melting transition leading to an effective hysteresis.[17]

The equilibrium phase diagrams of lead and aluminum show that they are immiscible;[18] transmission electron microscopy[19] and x-ray-diffraction[20] studies of aluminum implanted with lead revealed that the lead atoms cluster into precipitates which are aligned epitaxially with the aluminum matrix. Samples with Pb precipitates have also been prepared by rapid solidification.[21]

A (111)-cut aluminum single crystal (9 mm diam, 1 mm thick) was prepared by mechanical and electrolytical polishing. Subsequently a strip 4 mm wide was implanted with Pb^+ at an energy of 150 keV to a fluence of 2×10^{16} cm^{-2}. The beam spot was defined by a slit of size 2×1.5 mm^2, the total beam current was 0.9 μA, and the sample was translated behind the slit in two parallel scans at a speed of 0.0142 mm/s. During implantation the sample temperature was less than 330 K.

The implanted samples were studied by x-ray diffraction, using a rotation anode (Cu $K\alpha$) operated at 150 mA, 50 kV. The diffractometer was equipped with a fifth circle allowing for the use of two scattering planes, one containing the Al(111) and Al(002) reflections and a second the Al(111) and Al(220) ones. The sample was mounted with silver paste on the copper base of a small furnace, and kept under vacuum conditions using a standard diffusion pump. The temperature was controlled with a relative stability of 0.3 K and it was measured using a Chromel-Alumel thermocouple imbedded in the copper base. In order to check if there was a temperature gradient from the front of the sample to the copper base a second thermocouple was mounted at the front of an unimplanted sample. This second thermocouple could not be used during the diffraction measurements as it would block the x-ray beam. The temperature at the sample surface was always slightly lower than at the copper base, but never more than 3 K, obtained at 700 K.

Diffraction from the lead inclusions was studied during three heating and cooling sequences, and x-ray measurements were performed at fixed temperatures. The

Pb(111) peak was scanned in three directions in q space, namely along the longitudinal [111] direction (x scan), the transverse [11$\bar{2}$] direction (y scan), and transverse [$\bar{2}$20] direction (z scan); see Fig. 1. The time required to perform these scans was 70 min and the time for a complete temperature sequence was 1-2 weeks. To test the stability of the superheated and supercooled phases the furnance was kept for 21 h at 618 K (superheated) and for 35 h at 588 K (supercooled). During these tests, the superheated and the supercooled phases prevailed unaltered.

Hysteresis across the melting transition is clearly seen in Fig. 2 where the integrated intensities from the first and third temperature sequences are shown. During the first heating sequence, superheating is observed up to 67 K above the bulk melting point T_B (601 K[18]), and solidification begins 21 K below T_B. In the third heating sequence, superheating is observed up to 44 K above T_B, and solidification begins 18 K below. The mean sizes of the precipitates at the beginning of the three heating sequences were 140, 210, and 270 Å, respectively.[22] We hence ascribe the observed narrowing of the hysteresis loop to be due to this growth. At room temperature the lattice parameter of Pb determined from the position of the Pb(111) Bragg peak was 4.954 ± 0.004 Å and the tabulated bulk value is 4.9505 Å.[23] At the bulk melting temperature T_B we measured a lattice parameter for the precipitates of 4.993 ± 0.004 Å compared with a calculated bulk value of 4.9957 Å.[24] The compressibility of lead is 2.2×10^{-11} Pa^{-1} (Ref. 18) and we hence estimate the overpressure of the Pb precipitates at T_B to be at the most 0.18 GPa. Using the Clausius-Clapeyron equation $dp/dT = L/T\Delta V$,[25] where p is the pressure, T is the absolute temperature, $L = 4.81$ kJ/mol is the latent heat of fusion, and $\Delta V = 0.035$ is the relative volume change,[18] $dp/dT = 0.0129$ GPa/K. The upper bound on the pressure 0.18 GPa corresponds to a 14-K increase in the melting temperature. This cannot account for the superheating of 67 K, and 44 K observed in the first and third temperature sequences.

The melting transition for precipitates in a confined volume may be pressure broadened; i.e., melting may take place over a finite-temperature interval where the solid and liquid phases coexist. In this interval the pressure can be estimated from the measured lattice parameter of the solid fraction. During the first melting a gradual increase in the pressure up to 0.16 GPa was observed. However, no such pressure increase was observed during the subsequent melting. A pressure of 0.16 GPa corresponds to an increase in the melting point of 12 K. Uhlmann[5] has given a thermodynamic estimate of the superheating required in order to nucleate the fluid phase in a material confined by a rigid cavity. The required superheating for lead is 17 K.[26]

In bulk crystals, it is a general empirical observation (the Lindemann criterion[27]) that melting takes place when the root-mean-square (rms) displacements of the atoms exceed roughly a tenth of the nearest-neighbor distance. These displacements are reflected in the Debye expression for the integrated intensity $I = I_0 \exp(-2M)$, M is proportional to the absolute temperature T and I_0 is a constant.[28] Figure 3 shows a logarithmic plot of the integrated intensity for the Pb(111) and Pb(222) peaks from the third heating sequence. Fitting a straight line to the data from 297 to 573 K, we find $2M = 0.0010T$ and $2M = 0.0035T$ for the Pb(111) and Pb(222) reflections, respectively. The ratio of these two values is 3.5 which compares reasonably well with the expected value of 4. Figure 4 shows the rms displacements $\langle u_x^2 \rangle^{1/2}$

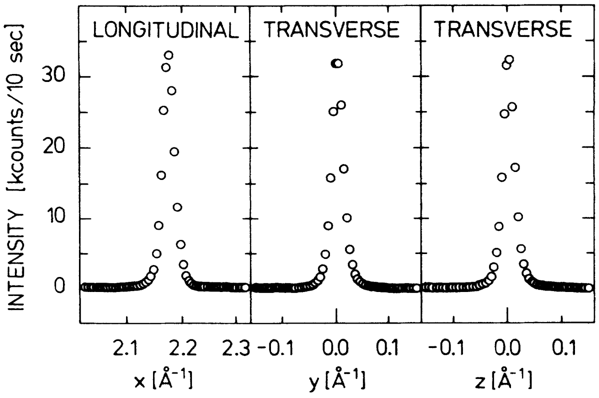

FIG. 1. Scan of the Pb(111) peak in three mutually orthogonal directions: the longitudinal [111] (x scan), transverse [11$\bar{2}$] (y scan), and transverse [$\bar{2}$20] direction (z scan). The temperature was 583 K.

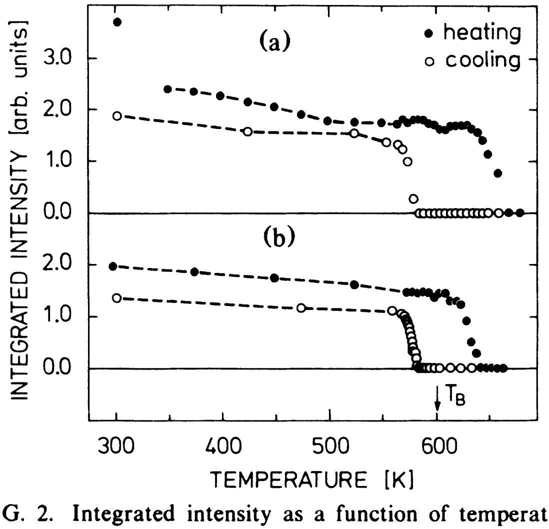

FIG. 2. Integrated intensity as a function of temperature, for the (a) first and (b) third temperature sequences. Solid and open circles represent data obtained during heating and cooling, respectively. The arrow T_B marks the bulk melting point of lead (Ref. 18). In the first heating sequence, superheating prevails to 67 K above T_B and solidification begins 21 K below T_B. In the third heating sequence superheating prevails to 44 K above T_B and solidification begins 18 K below the bulk melting point.

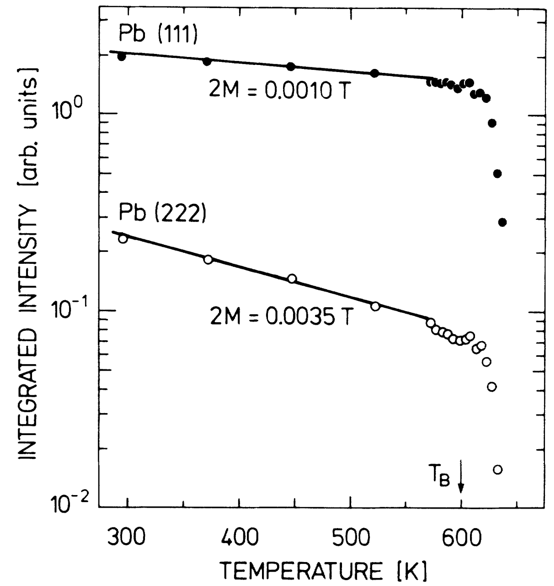

FIG. 3. Logarithmic plot of the integrated intensity for the Pb(111) and Pb(222) peaks from the third heating sequence. The melting temperature for bulk lead is marked by the arrow T_B (Ref. 18). Fitting the Debye expression $I = I_0 \exp(-2M)$ to the data obtained in the temperature interval 297-573 K, we find $2M = 0.0010T$ and $2M = 0.0035T$, respectively.

$= [\ln(I/I_0)]^{1/2}/Q$ of the lead atoms; I is the integrated intensity and Q is the momentum transfer.[28] Until melting begins at 626 K (see Fig. 2) the rms displacements (solid circles) of the Pb atoms increase slowly to a value equal to 12% of the nearest-neighbor distance. At temperatures above 626 K where some of the Pb is melted not all atoms contribute to the observed integrated intensity and, consequently, the calculated rms values are unphysical.

Large superheating is generally not observed during melting of metals. Therefore, it is plausible that the superheating seen here is due to the lack of a free surface. The fact that indirect evidence for surface initiated melting could be obtained by the study of surface-coated crystals was suggested in a study of gold-coated silver crystals.[29] Based on room-temperature measurements of chemical composition profiles, it was concluded that superheating had been maintained for 1 min. As gold and silver atoms interdiffuse, the particles were subject to a continuous alloying process and thereby to various unknown dynamical effects, e.g., to an effective pressure. In a recent paper[30] it is shown that a shallow epitaxial layer of PbO on a lead (110) surface suppresses premelting. For a confined solid, a possible contribution to the superheating is the extra stability of the solid phase caused by the epitaxial alignment of the precipitates and the host matrix. Further, for a "surface" initiated melting process, an increase in melting temperature may, in addition, be caused by the extra energy it takes to expel a Pb atom to the host matrix, in comparison with the energy needed to create a vacancy at a free surface. Both of these mechanisms will be more pronounced for the smaller precipitates, because of the larger surface-to-volume ratio.

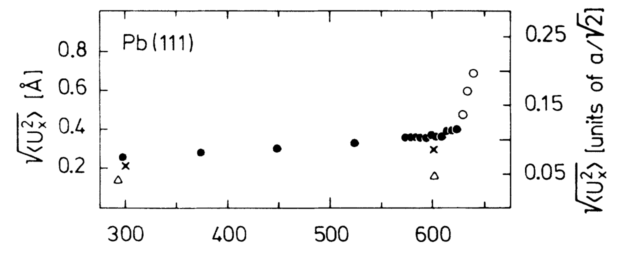

FIG. 4. Experimentally determined root-mean-square (rms) displacement of the lead atoms as a function of temperature. Up to the melting temperature at 626 K, the rms values (solid circles) slowly increased to 12% of the nearest-neighbor distance. Above 626 K a fraction of the precipitates are melted, and, consequently, the rms values shown (open circles) are unphysical. Also shown in the figure are rms values for bulk lead (crosses) and rms values for bulk aluminum (triangles) (Ref. 32).

If we consider the lattice vibrations in Fig. 4, we find that melting sets in when the rms displacements are 12% of the nearest-neighbor distance. This is in good agreement with the Lindemann criterion. Our measured rms displacements in the Pb precipitates are slightly larger than in bulk lead (see Fig. 4). However, the difference in the rms values is probably not larger than our systematic uncertainties.

In addition to the superheating discussed above, the lead precipitates also exhibit a significant supercooling of 21 and 18 K, respectively. At first one might think that the confinement of the lead precipitates by plane surfaces would help nucleation of the solid phase, but apparently this is not the case. Presumably, the interphase energy of lead and aluminum is so high that the walls confining the precipitates play a minor role in the solidification. We therefore suggest that the observed supercooling is a consequence of the size of the Pb precipitates. In order to start nucleation in a supercooled liquid, a nucleation grain of a certain size is needed, and the minimum size of the nucleation grain reduces with increased supercooling of the liquid. Using free-energy considerations it is found that the critical size of nucleation is given by the following expression $d = 4\gamma_{SL} T_B / L\Delta T$,[31] where $\gamma_{SL} = 33.3$ mJ/m^2 (Ref. 31) is the interface energy between solid and liquid lead and ΔT is the supercooling. At the end of the first and third heating sequences the mean size of the precipitates was 210 and 270 Å, respectively. Using this as the size of the critical nucleus of solidification the above expression gives corresponding supercoolings of 14 and 11 K, respectively. These values are slightly smaller than the 21- and 18-K supercooling observed for the lead precipitates.

In conclusion, our *in situ* study gives unambiguous evidence for a thermal hysteresis loop across the melting and solidification transition of lead inclusions in aluminum. The accurate measurements of the lattice constant show that the increacse in melting temperature for the lead in the precipitates is not due to high pressure in the precipitates; instead it must be due to the nature of the Al-Pb interface. The size of the precipitates at the observed supercooling agrees well with the critical size for nucleation. That is, only when the critical size for nucleation is smaller than the size of the Pb precipitates do the precipitates solidify.

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[1] For a review, see R. M. J. Cotterill, in *Ordering in Strongly Fluctuating Condensed Matter Systems,* edited by T. Riste (Plenum, New York, 1980).

[2] For a discussion, see N. F. Mott, Proc. Roy. Soc. London A **215**, 1 (1952).

[3] R. M. J. Cotterill and J. U. Madsen, Phys. Rev. B **33**, 262 (1986).

[4] For a review, see J. F. van der Veen, B. Pluis, and A. W. D. van der Gon, in *Chemistry and Physics of Solid Surfaces,* edited by R. Vanselow and R. Howe (Springer-Verlag, Berlin, 1988), Vol. VII.

[5] D. R. Uhlmann, J. Non-Cryst Solids **41**, 347 (1980).

[6] J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955).

[7] R. M. J. Cotterill, Philos. Mag. **32**, 1283 (1975).

[8] W. Schommers, Phys. Rev. B **32**, 6845 (1985).

[9] E. Haykin and N. P. Bénet, C. R. Acad. Sci. USSR **23**, 31 (1939).

[10] J. W. M. Frenken and J. F. van der Veen, Phys. Rev. Lett. **54**, 134 (1985).

[11] B. Pluis, A. W. Denier van der Gon, J. W. M. Frenken, and J. F. van der Veen, Phys. Rev. Lett. **59**, 2678 (1987).

[12] Ph. Buffat and J.-P Borel, Phys. Rev. A **13**, 2287 (1976).

[13] H. Saka, Y. Nishikawa, and T. Imura, Philos. Mag. A **57**, 895 (1988).

[14] R. H. Willens, A. Kornblit, L. R. Testardi, and S. Nakahara, Phys. Rev. B **25**, 290 (1982).

[15] R. Garrigos, R. Kofman, P. Cheyssac, and M. Y. Perrin, Europhys. Lett. **1**, 355 (1986).

[16] G. D. T. Spiller, Philos. Mag. A **46**, 535 (1982).

[17] R. S. Berry and D. J. Wales, Phys. Rev. Lett. **63**, 1156 (1989).

[18] *Smithells Metals Reference Book,* edited by E. A. Brandes (Butterworths, London, 1983).

[19] P. A. Thackery and R. S. Nelson, Philos. Mag. **19**, 169 (1969).

[20] L. Gråbaek, J. Bohr, E. Johnson, H. H. Andersen, A. Johansen, and L. Sarholt-Kristensen, Mater. Sci. Eng. A **115**, 97 (1989).

[21] K. I. Moore, K. Chattopadhyay, and B. Cantor, Proc. Roy. Soc. London A **414**, 499 (1987).

[22] The mean size was calculated from the FWHM values deconvoluted for the experimental resolution.

[23] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1963), Vol. 1.

[24] This was calculated using tabulated values for the coefficient of thermal expansion of lead, $\alpha_{\mathrm{Pb}}=2.91\times10^{-5}$ (RT → 373 K), $\alpha_{\mathrm{Pb}}=3.00\times10^{-5}$ (373 → 473 K), and $\alpha_{\mathrm{Pb}}=3.13\times10^{-5}$ (473 → T_B K) (Ref. 18).

[25] L. D. Landau and E. M. Lifshitz, *Course on Theoretical Physics: Statistical Physics* (Pergamon, Oxford, 1980), Vol. 5, Pt. 1, pp. 255 and 256.

[26] $\Delta G_{ST,V}=2G_C K_L(\Delta V)^2/(3K_L+4G_C)$ and $\Delta TT>\Delta G_{ST,V}\times LT_B^2$ (Ref. 5), $G_C=1/S_{44}=1/68.0$ TPa (Ref. 18), and $K_L=1/\kappa=1/0.0275$ GPa from *Gmelins Handbuch der Anorganischen Chemie* (Verlag Chemie, Weinheim/Bergstrasse, 1972).

[27] F. A. Lindemann, Z. Phys. **14**, 609 (1910).

[28] A. Guinier, *X-Ray Diffraction, in Crystals, Imperfect Crystals and Amorphous Bodies* (Freeman, San Francisco, 1963).

[29] J. Daeges, H. Gleiter, and J. H. Perepezko, Phys. Lett. A **119**, 79 (1986).

[30] A. W. Denier van der Gon, B. Pluis, R. J. Smith, and J. F. van der Veen, Surf. Sci. **209**, 431 (1989).

[31] D. A. Porter and K. E. Easterling, *Phase Transformations in Metals and Alloys* (Van Nostrand Reinhold, Wokingham, U.K., 1981), pp. 171 and 186–198.

[32] *International Tables for X-Ray Crystallography,* edited by N. F. M. Henry and K. Lonsdale (The International Union of Crystallography, Birmingham, U.K., 1965).