

Melting of indium at high pressure determined by monochromatic x-ray diffraction in an externally-heated diamond anvil cell

Guoyin Shen,^{a)} Nagayoshi Sata, Mark L. Rivers,^{b)} and Stephen R. Sutton^{b)}
Consortium for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60637

(Received 2 February 2001; accepted for publication 2 April 2001)

The melting behavior of indium at high pressure has been studied in an externally heated diamond anvil cell (DAC) using x-ray diffraction measurements. Melting at high pressure was identified by the appearance of diffuse scattering from the melt with the simultaneous disappearance of crystalline diffraction signals. The observed melting curve is in good agreement with previous determinations based on resistivity measurements in a piston cylinder apparatus. These results demonstrate the successful melting experiments in a DAC using the x-ray diffuse scattering as the melting criterion. © 2001 American Institute of Physics. [DOI: 10.1063/1.1374497]

Melting is an important phenomenon for solids, characterized by the loss of long-range order and resistance to shear. In recent years, the generation and measurement of simultaneous high pressures and high temperatures has undergone rapid development with the diamond anvil cell (DAC) technique.^{1–3} The amount of available data on melting behavior at high pressure is increasing. However, at high pressures, detection of the onset of melting is challenging. The difficulties lie in the characterization of small samples (e.g., unambiguously melting criteria) and in the measurement of P and T under extreme conditions. For example, considerable controversy has surrounded the determination of the melting temperature of iron at $P > 20$ GPa with DAC experiments.^{4,5} The melting determination in DAC experiments has been a subject of many articles.^{6–11}

Recently, x-ray diffraction with the energy dispersive technique has been combined with the DAC and used for melting determination.^{12,13} The appearance of diffraction peaks at a certain P – T condition undoubtedly indicates the presence of a crystalline phase. However, the loss of the diffraction peaks is not necessarily indicative of melting, due to possible crystal growth at high T , resulting in few crystallites in the small sample volume. In this study, angle dispersive diffraction was employed with an area detector for collecting the x-ray scattering signals. Using an area detector enables one to identify melting unambiguously by the observation of diffuse scattering from the melt with the simultaneous disappearance of all crystalline diffraction peaks.

An externally heated DAC (DXR-7, Diacell) was used in this study. The main feature of the DAC design is the use of four cartridge heaters inserted in the cell, providing heat to the whole cell and resulting in a uniform temperature distribution inside the cell. Temperatures were measured by a type-K thermocouple at the gap position between the gasket and the diamond anvil. Prior to the experiment, a second thermocouple was placed at the sample position, and, in this way, the temperature at the sample position was found to be 4.5 K less than that at the gap position with a standard de-

viation of 1.9 K. Indium powder (99.999%, Alfa Aesar) was loaded into the rhenium gasket aperture (100 μm in diameter and 30 μm thick). NaCl was used as the pressure transmitting medium and the internal calibrant for pressure measurement.

The x-ray diffraction experiment was performed at GeoSoilEnviro CARS, beamline 13-BM-D at the Advanced Photon Source. A charge coupled device (CCD) detector (Bruker-2K) was used to collect diffraction patterns. The monochromatic x-ray beam was produced using a channel-cut crystal (silicon 220) and was fixed at an energy of 29.200 keV, calibrated by scanning through the tin metal absorption edge. The x-ray beam size was controlled by a slit system to 150 \times 150 μm and then focused to a beam size of 7(vertical) \times 10(horizontal) μm full width at half maximum by Kirkpatrick–Baez mirrors.¹⁴ Typical CCD exposure times were 5 min.

Figure 1 shows recorded diffraction patterns at ~ 2 GPa near the onset of melting. The two diffraction rings that are present in all three images are NaCl–B1 (200) and (220) lines, respectively. When the temperature was raised to 519 K, the crystalline nature of indium was still clearly identified [spotty pattern in Fig. 1(a)]. As the temperature was increased to 526 K, we observed that the indium diffraction spots faded out and diffuse scattering appeared in the vicinity of the indium (101) diffraction [Fig. 1(b)]. When the temperature was raised to 531 K, the scattered diffuse area [Fig. 1(b)] became a homogeneous broad ring [Fig. 1(c)] accompanied by the disappearance of all diffraction spots from indium, indicating a completely molten state. Upon slight cooling, to 523 K, the homogeneous broad ring disappeared, and the diffuse scattering was now distributed only in some localized areas. These diffuse scattering areas persisted down to 475 K. Note that this temperature is below the point (519 K) where the crystalline state was observed on increasing temperature [Fig. 1(a)], which indicates some hysteresis during the sample solidification. Diffraction spots of indium reappeared at temperatures below 475 K.

The CCD images were integrated using the software FIT2D as a function of diffraction angle 2θ . The broad diffuse ring is clearly seen in the integrated pattern as a broad band centered near $9^\circ 2\theta$ [Fig. 1(d)]. The area of this broad peak

^{a)}Electronic mail: shen@cars.uchicago.edu

^{b)}Also at: Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637.

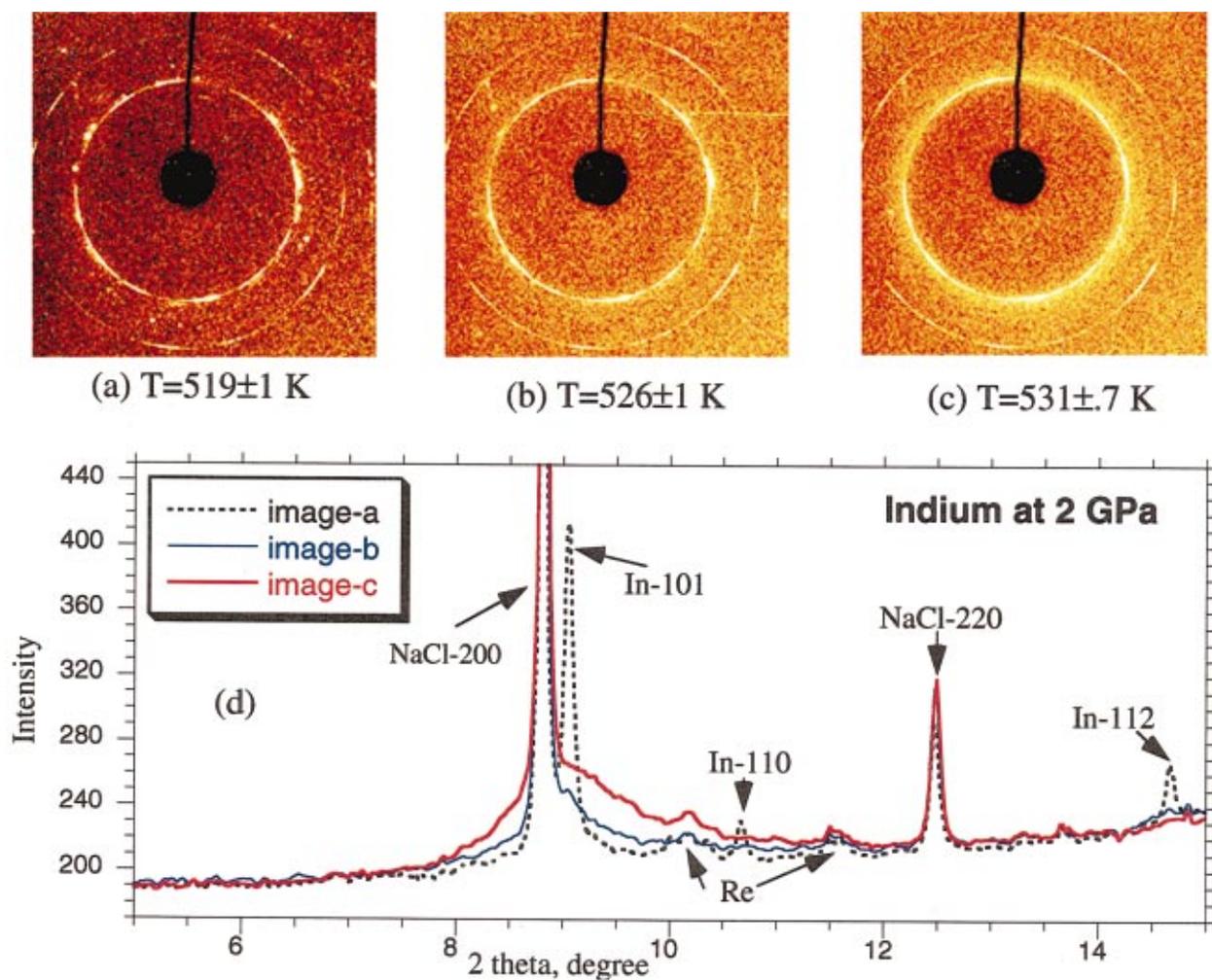


FIG. 1. (Color) X-ray scattering images and their integrated pattern at the onset of melting of indium at about 2 GPa. Two sharp rings are the diffraction of NaCl. (a) Crystalline indium shows a spotty pattern. (b) The indium diffraction spots fade out and diffuse scattering appears. (c) A clear homogeneous diffuse ring of the melt can be seen. (d) Integrated patterns by FIT2D for images from (a) to (c). A broad diffuse band can be clearly seen in the vicinity of indium (101).

was calculated by using a peak-fitting program (PEAKFIT). A linear background and Voigt function for the band were used in the fitting. Figure 2 shows the area of the diffuse band as a function of temperature near the melting point. As the temperature is increased, there is a sharp increase in intensity of the diffuse scattering upon melting over a temperature interval of about 6 K. Upon slight cooling, the intensity of the diffuse scattering drops rapidly in the same region where the sharp change occurred on increasing temperature. This means that the solid-liquid transition is reversible with negligible hysteresis within the temperature precision of this study. Therefore, the sharp change in intensity signifies melting and the temperature interval over which the transition takes place is a measure of the uncertainty in the melting point determination. As the temperature was further decreased, we found that indium did not show crystalline diffraction immediately below melting point. Some hysteresis in the intensity occurred at the bottom of the sharp change as can be seen from Fig. 2. From x-ray scattering images, the diffuse scattering was neither a broad homogeneous ring from the melt [Fig. 1(c)] nor a sharp crystalline pattern [Fig. 1(a)], instead showing scattered intensity in some areas around the ring [similar to Fig. 1(b)]. The hysteresis ex-

tended to a temperature of about 50 K below the melting point. Since it is generally assumed¹⁵ that the melt consists of a randomly close-packed lattice with about 10% vacancies with respect to the crystal lattice, the hysteresis could arise from diffuse scattering due to the significant number of vacancies sustained upon cooling. It could be also a kinetic effect due to difficulty of nucleating crystals.

The melting of indium at high pressure has previously been studied based on an observation of a sharp change in resistivity using piston cylinder apparatus.¹⁶⁻¹⁸ Our result is shown in Fig. 3 compared to the results of Dudley and Hall¹⁶ and McDaniel and co-workers.¹⁷ At pressures near 3 GPa, our data show a slightly higher melting temperature than those of Dudley and Hall.¹⁶ As pointed out in a later work,²⁰ the pressure scale in Dudley and Hall's work¹⁶ needs to be revised downward in accordance with the fixed points of solid-solid transitions obtained by Kennedy and LaMori.¹⁹ After pressure correction, the melting curve of Dudley and Hall¹⁶ is almost identical to that of McDaniel and co-workers.¹⁷ Clearly, our data support the correction.²⁰

In conclusion, we have demonstrated that the melting of samples in the DAC can be clearly detected by the appearance of diffuse x-ray scattering from the melt and the simul-

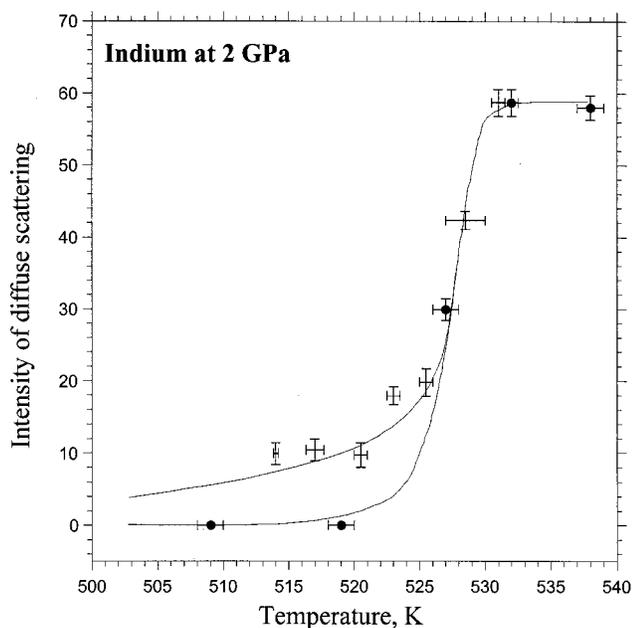


FIG. 2. Intensity change of the diffuse scattering band at the onset of melting. Solid circles are the data upon heating; while the crosses are those on cooling. A sharp change in intensity occurs in the same temperature region upon both heating and cooling, indicating the transition is reversible. Lines are freehand fits to the heating and cooling paths. The hysteresis of complete solidification appears at the low temperature side of the sharp transition. Error bars for temperature are from the multiple measurements during the exposure of 5 min. Errors for the intensity of diffuse scattering are obtained from the standard errors in fitting the band with >95% confidence limits.

taneous disappearance of all crystalline x-ray diffraction signals from the sample. The diffuse scattering of the melt showed a broad homogeneous ring in the recorded diffraction pattern, providing a clear indication of the presence of the melt. The melting is found to be reversible upon heating and cooling, though complete solidification on cooling showed some hysteresis. The current method provides an objective way of identifying melting, an important extension of the visual observation methods generally used in previous DAC studies. This technique, utilizing an area detector and micro-x-ray beam, should be applicable to many other high pressure melting studies, such as laser heated DAC experiments on melting at ultrahigh pressures.

The authors thank Emmanuel Soignard, Peter Eng, Takeyuki Uchida, Fred Sopron, Mike Jagger, and Nancy Lazarz for the assistance during the experiment. Comments from Dr. Tom Duffy improved the manuscript. This work is supported by NSF-EAR 00011498. The GSECARS sector is supported by the National Science Foundation (Earth Sciences Instrumentation and Facilities Program) and the Department of Energy-Basic Energy Sciences (Geosciences Program).

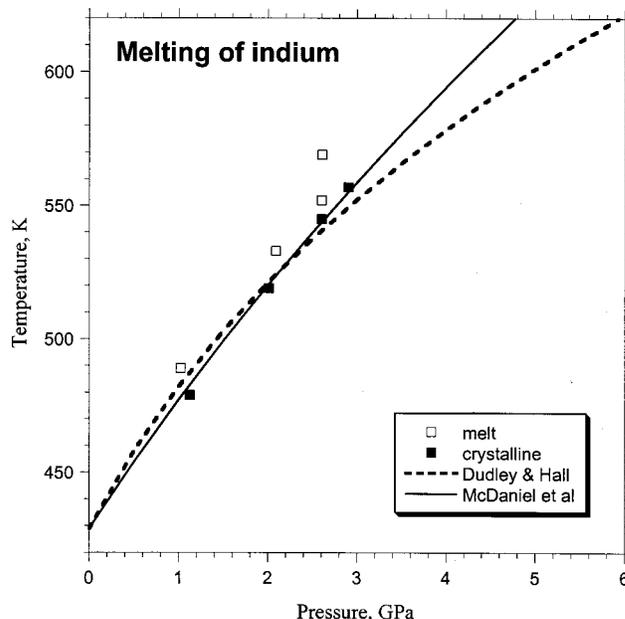


FIG. 3. High pressure melting curves for indium. Symbols are the results of this study with error bars comparable or less than the symbol size. The data agree well with those of Dudley and Hall (Ref. 16) (after pressure correction, see text) and McDaniel and co-workers (Ref. 17) based on resistivity measurements in piston cylinder apparatus.

- ¹R. Boehler, *Rev. Geophys.* **38**, 221 (2000).
- ²H. K. Mao and R. J. Hemley, *Philos. Trans. R. Soc. London, Ser. A* **354**, 1315 (1996).
- ³G. Shen, M. L. Rivers, Y. Wang, and S. J. Sutton, *Rev. Sci. Instrum.* **72**, 1273 (2001)
- ⁴Q. Williams, R. Jeanloz, J. Bass, B. Svendsen, and T. J. Ahrens, *Science* **236**, 181 (1987).
- ⁵R. Boehler, *Nature (London)* **363**, 534 (1993).
- ⁶O. L. Anderson and A. G. Duba, *J. Geophys. Res.* **102**, 22 659 (1997).
- ⁷R. Boehler, *Annu. Rev. Earth Planet Sci.* **24**, 15 (1996).
- ⁸A. G. Duba, in *High Pressure Science and Technology*, edited by S. C. Schmidt, J. W. Shaner, G. A. Samara, and M. Ross (AIP Press, New York, 1994), pp. 923–926.
- ⁹R. Jeanloz and A. Kavner, *Philos. Trans. R. Soc. London, Ser. A* **354**, 1279 (1996).
- ¹⁰A. P. Jephcoat and S. P. Besedin, *Philos. Trans. R. Soc. London, Ser. A* **354**, 1333 (1996).
- ¹¹P. Lazor and S. K. Saxena, *Philos. Trans. R. Soc. London, Ser. A* **354**, 1307 (1996).
- ¹²C. S. Yoo, J. Akella, A. Campbell, H. K. Mao, and R. J. Hemley, *Science* **270**, 1473 (1995).
- ¹³G. Shen, H. K. Mao, R. J. Hemley, T. S. Duffy, and M. L. Rivers, *Geophys. Res. Lett.* **25**, 373 (1998).
- ¹⁴P. J. Eng, M. Newville, M. L. Rivers, and S. R. Sutton, *Proc. SPIE* **3449**, 145 (1998).
- ¹⁵A. R. Ubbelohde, *The Molten State of Matter* (Wiley, New York, 1978).
- ¹⁶J. D. Dudley and H. T. Hall, *Phys. Rev.* **118**, 1211 (1960).
- ¹⁷M. L. McDaniel, S. E. Babb, Jr., and G. J. Scott, *J. Chem. Phys.* **37**, 822 (1962).
- ¹⁸V. E. Fadeev, *J. Phys. Chem.* **45**, 1051 (1971).
- ¹⁹G. C. Kennedy and P. N. La Mori, *Progress in Very High Pressure Research* (Wiley, New York, 1961).
- ²⁰A. Jayaraman, W. Klement, Jr., R. C. Newton, and G. C. Kennedy, *J. Phys. Chem. Solids* **24**, 7 (1963).