High-pressure Melting of Iron Determined by X-ray Scattering

G. Shen, V.B. Prakapenka, M.L. Rivers, S.R. Sutton

Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL, U.S.A.

Introduction

The high-pressure melting of iron has been studied extensively [1-3] because it provides a first-order constraint on the temperature of the core. Estimates rely on the assumption that the boundary between the solid inner core and the liquid outer core is at the melting temperature of the core material.

However, considerable controversy has surrounded the determination of the melting temperature of iron, particularly at pressures above 30 GPa. One critical issue is the melting criterion. Melting is thermodynamically defined as equilibrium between a solid and a liquid. When materials melt, their physical properties, such as density, viscosity, absorption properties, and electrical resistance, change suddenly. Such property changes are characteristic of a first-order phase transition and are often used for recognition of melting. Different from other first-order phase transitions, melting is characterized by the loss of long-range order and resistance to shear. To definitively identify melting, one or both of these two characteristics should be documented. There are five types of melting criteria in laser-heated diamond anvil cell (DAC) experiments: fluid flow, glass formation, quench texture, change in sample properties, and the temperature versus laser power correlation. The observation of fluid flow is a good measure of the loss of resistance to shear. Therefore, it has been considered one of the best criteria and is widely used by almost all groups in the world. However, visual observation (fluid flow) is less obvious as pressure increases; above 30 GPa (where the lack of agreement starts), there is a large temperature gap of a few hundreds degrees between occasional small movement (not fluid flow) and fluidlike motion, making it difficult to unambiguously define the onset of melting. The subjective nature of visual observation may account for the inconsistent results in literature. Recently, an area detector with a monochromatic x-ray beam was successfully used for melting determination in a DAC. Melting at high pressure was identified by the appearance of diffuse scattering from the melt with the simultaneous loss of crystalline diffraction signals [4]. The new method relies on positive signals (diffuse scattering) together with a measure of the characteristic property of melting (loss of long-range order), providing an objective way of signifying melting and an important extension of the visual observation method. This report discusses the results of experiments on the melting of iron at pressures up to 58 GPa by using the x-ray scattering method.

Methods and Materials

Experiments were performed at GeoSoil-EnviroCARS (GSECARS) beamline station 13-ID-D at the APS. The iron sample (99.9+% purity, Alfa) was loaded in a DAC and heated under high pressure using a double-sided laser heating system [5]. The diamond anvil culet size was 500 μm in diameter. A hole of 200 μm in diameter was drilled at the center of a stainless steel gasket preindented to a thickness of 30 μm as a sample chamber. Iron powder was pressed into a disc to a thickness of ~10 μm. A flake of powder of ~50 μm in diameter was loaded in the sample chamber sandwiched with two dry NaCl layers (~10-μm thick) as pressure media as well as thermal insulating layers. The entire loading was in a glove box in an argon atmosphere to avoid any moisture. Cubic boron nitride seats were used in the DAC for hardness and x-ray transparency, resulting in a large opening angle for x-ray scattering. A monochromatic beam ($\lambda = 0.3311$ Å) was collimated by slits to a size of 150×150 μm^2 and then focused by a pair of Kirkpatrick-Baez mirrors to a size of 8 μm (vertical) × 10 (horizontal) at full width at half-maximum (FWHM). X-ray scattering was recorded by an on-line image plate system (MAR-345). The x-ray position was closely monitored by the x-ray luminescence signal arising from the NaCl layers and was aligned to the laser heating area where temperatures were measured. The collection time for x-ray scattering was 10 seconds. Previously developed experimental protocols [5] were utilized for stable laser heating over the data collection time, laser heating an area larger than the focused x-ray beam, and precise alignment between the laser heating spot and the x-ray beam. At each pressure, *in situ* x-ray diffraction/scattering patterns were acquired as the temperature was increased until clear diffuse scattering from the liquid was observed. Temperature was determined from thermal radiation spectra fitted to the Planck radiation law [5]. Pressure was determined at room temperature from x-ray diffraction patterns by using the equation of state of NaCl [6].
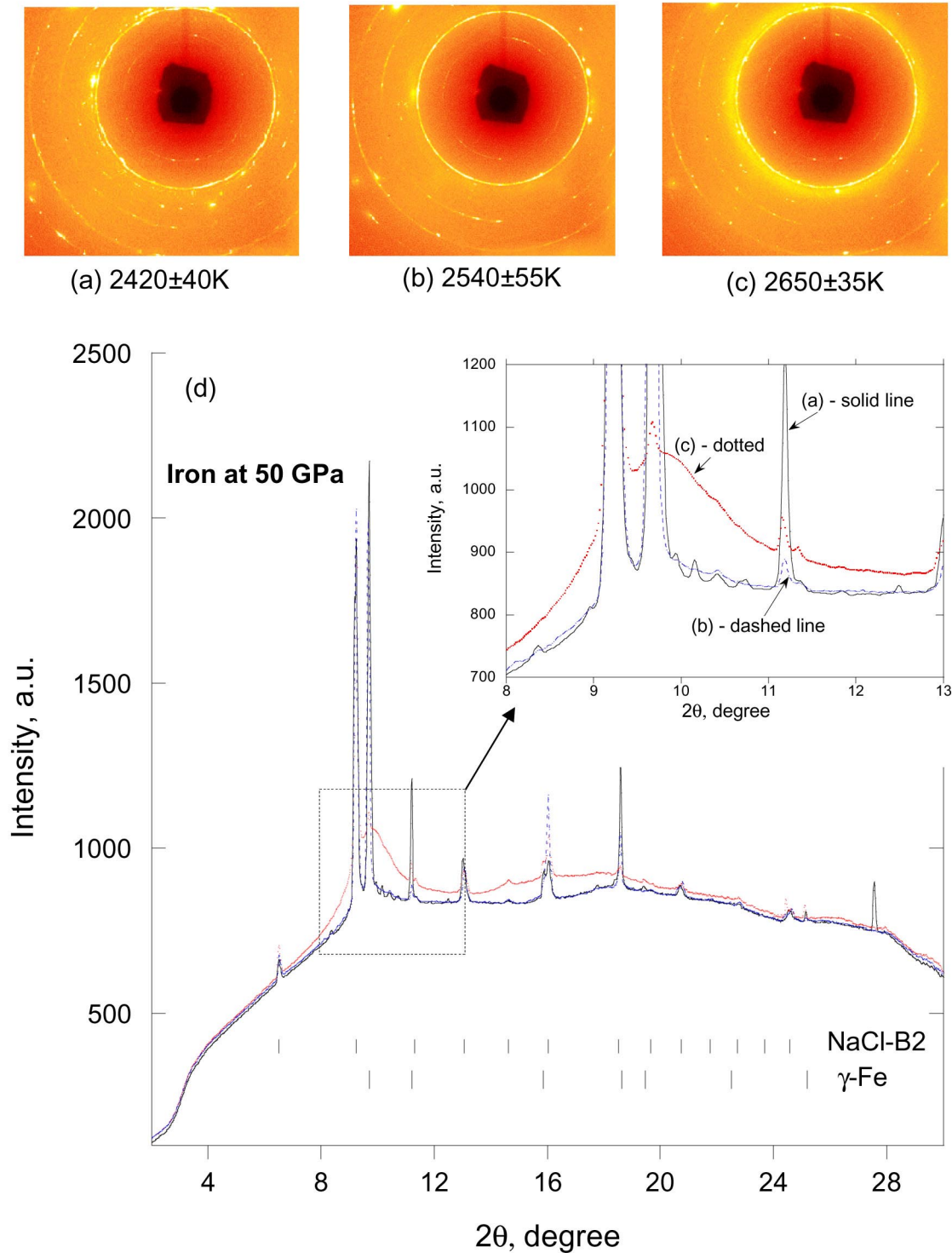
FIG. 1. X-ray diffraction/scattering patterns at 50 ±1 GPa. (a), (b), and (c) are x-ray diffraction/scattering images recorded at different temperatures; (d) shows integrated patterns corresponding to these images [(a) = dotted line, (b) = dashed line, and (c) = solid line]. The insert shows the major diffuse band region. Clear diffuse scattering from liquid iron is observed at 2650 ±35K. The crystalline phase below melting was found to be γ-Fe. Other crystalline diffraction lines arise from the pressure medium (NaCl-B2).

Results and Discussion

Figure 1 shows the measured x-ray diffraction/scattering patterns at 50 GPa. At a temperature of 2420 ±40K, crystalline diffraction from the fcc phase (γ-Fe) can be clearly observed [Fig. 1(a)]. After the temperature was increased to 2540 ±55K, diffuse scattering started to appear, with only a few diffraction spots from γ-Fe [Fig. 1(b)]. This temperature could be close to (just below) melting. Upon further increasing temperature to 2650 ±35K, a complete diffuse ring can be observed, reflecting the liquid state of iron at this pressure [Fig. 1(c)]. The change in x-ray diffraction/scattering from crystalline to liquid phases provides an unambiguous melting criterion as demonstrated in Fig. 1. Defining the onset of melting in a laser-heated DAC has been the subject of a long-standing debate. The method in this study provides an objective melting criterion, unlike the visual observations that are widely used. Note that for the iron in this study, melting is reversible, so the same sample can be used again in a single run at different pressures. For glass-forming materials, caution should be taken, attention should be paid to the experimental pressure-temperature paths.

In the covered pressure range, our data on melting temperatures are consistent with those from previous studies based on visual observations [2, 7] and x-ray diffraction with the energy-dispersive technique [3]. At the highest pressure of this study, the solid phase before melting was found to be γ-Fe, indicating that the previously determined γ–ε-l triple point (60 ±5 GPa, 2800 ±200K) [3] should be shifted to higher pressures. Note that the present data reflect the melting of γ-Fe. The melting of ε-Fe from using the x-ray criterion remains to be determined.

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