

Absolute temperature measurement in a laser-heated diamond anvil cell

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[1] The laser-heated diamond anvil cell has been widely used to study mineral physics under high pressure and temperature, and these studies have provided valuable information in understanding planetary interiors; however, use of the spectroradiometric method in the studies has raised concerns about the accuracy of obtained temperature values. We have built a laser-heating system coupled with nuclear resonant inelastic x-ray scattering to explore particular physical properties of deep-Earth materials. Energy spectra of iron were measured up to 58 GPa and 1700 K. The detailed balance principle applied to the inelastic x-ray scattering spectra provides absolute temperatures of the laser-heated sample. These temperatures are in very good agreement with values determined from the thermal radiation spectra fitted to the Planck radiation function up to 1700 K. Our data provide, for the first time, independent confirmation of the validity of temperatures determined from spectroradiometric method in the laser-heated diamond cell experiments. **INDEX TERMS:** 3924 Mineral Physics: High-pressure behavior; 3934 Mineral Physics: Optical, infrared, and Raman spectroscopy; 3939 Mineral Physics: Physical thermodynamics; 3954 Mineral Physics: X ray, neutron, and electron spectroscopy and diffraction; 3994 Mineral Physics: Instruments and techniques. **Citation:** Lin, J.-F., W. Sturhahn, J. Zhao, G. Shen, H. Mao, and R. J. Hemley (2004), Absolute temperature measurement in a laser-heated diamond anvil cell, *Geophys. Res. Lett.*, *31*, L14611, doi:10.1029/2004GL020599.

1. Introduction

[2] Static high-pressure and high-temperature experiments have provided very valuable information in understanding planetary materials deep in the Earth's interior. In particular, the laser-heated diamond anvil cell (LHDAC) technique has been the most productive method to reach ultrahigh static pressure and temperature conditions ($P > 100$ GPa and $T > 3000$ K) found deep in planetary interiors [Ming and Bassett, 1974; Bassett, 2001; Shen et al., 2001]. Since the birth of the LHDAC in the late 1960s [Ming and Bassett, 1974; Bassett, 2001], the LHDAC technique has been widely used with in situ x-ray diffraction, melting point studies by observing melting features, and chemical

analyses of the quenched sample [Boehler, 1986; Boehler and Chopelas, 1991; Lazor et al., 1993; Jeanloz and Kavner, 1996; Dewaele et al., 2000; Shen et al., 1998, 2001]. In situ x-ray diffraction studies of materials deep in the Earth's mantle and core have advanced our understanding of the Earth's interior [Hemley et al., 2000, and references therein]. These studies have yielded data on the phase diagram, equation of state, elasticity, composition, and melting curve of planetary materials.

[3] The spectroradiometric method for temperature measurement has been widely used in LHDAC experiments in which thermal emission from the laser-heated sample was collected by a detector through an optical system and then fitted to the Planck radiation function [Heinz and Jeanloz, 1987; Heinz et al., 1991]. Although the accuracy and precision of the temperature measurement in the LHDAC have been tested using various methods such as a second known radiation point, melting of a metal foil with known melting temperature at ambient conditions, and a thermocouple, the unknown wavelength dependence of emissivity and chromatic aberrations together with possible temperature gradients have raised concerns over the accuracy of obtained temperature values [Boehler, 1986; Heinz and Jeanloz, 1987; Heinz et al., 1991; Jephcoat and Besedin, 1996]. An independent and absolute temperature calibrant in the LHDAC is thus necessary to validate the reliability of the spectroradiometric method. Similarly, the reliability of pressure standards is a key issue to all high-pressure research. The search for a primary high-pressure scale has been ongoing for decades. Recently, simultaneous measurements of the sound velocities and the compressibility of NaCl and MgO have been used to derive a primary high-pressure scale [Mueller et al., 2003] and to confirm the reliability of the other secondary pressure standards such as the ruby pressure scale [Zha et al., 2000].

[4] In principle, the absolute temperature of the heated sample can be independently determined from the intensity ratios of the lattice excitation energy pairs, phonon creation and annihilation. Recently, this method of using the detailed balance principle has been applied to determine the average temperature of a laser-heated sample based on temperature-dependent intensity asymmetry of the Raman spectra using transparent CO₂ as an example [Lin et al., 2004; Santoro et al., 2004]; however, the studies do not provide independent validation of the spectroradiometric method. The nuclear resonant inelastic x-ray scattering (NRIXS) technique provides a direct probe of the energy spectra of the resonant isotope [Sturhahn et al., 1995; Hu et al., 2003; Sturhahn, 2004], e.g., using the 14.4125 keV transition of ⁵⁷Fe. Phonon density of states (DOS) of hexagonal close-packed (hcp) Fe have been studied up to 153 GPa at 300 K [Mao et

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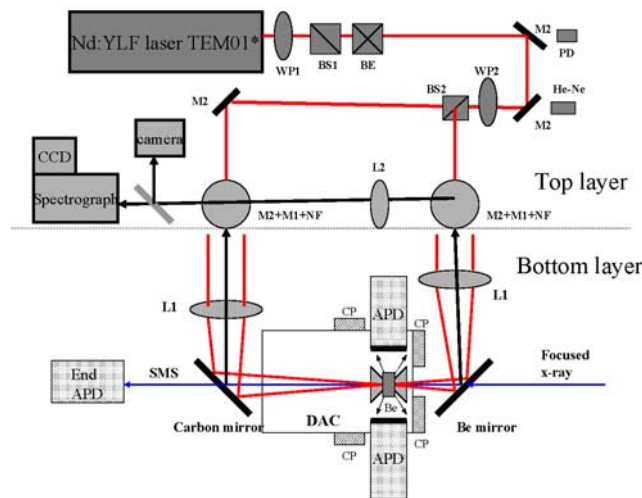


Figure 1. Schematic of the double-sided laser heating system combined with NRIXS technique at sector 3 of the Advanced Photon Source. The system was built in two layers, top and bottom. A continuous wave Nd:YLF laser beam in TEM₀₁ mode (donut mode) with a maximum output power of 80 Watts was regulated by the wave plate (WP1) and polarized beamsplitter (BS1). The laser beam was split into two laser beams by the second set of wave plate and polarized beamsplitter (WP2 and BS2) which were also used to balance the laser power between upstream and downstream sides. The laser beams were then focused onto $\sim 40\ \mu\text{m}$ at the sample. An upstream beryllium mirror coated with gold and a downstream carbon mirror coated with silver were used to guide the laser beam and to reflect the thermal radiation. The wide-angle DAC was constantly cooled by the attached cooling plates (CP) insuring the stability of the cell temperature and the sample position during laser heating. The front entrance of each APD detector was covered with a thin Be window to protect the device from light. The Fe K-fluorescence radiation was collected by three APDs surrounding the DAC. The fourth APD in transmission was used to record synchrotron Mössbauer spectroscopic (SMS) signal. Red line: YLF laser; blue line: x-ray; black line: white light/thermal emission. WP and BS: wave plate and polarized beamsplitter to regulate the Nd:YLF laser; BE: beam expander; M2: dichroic laser mirror reflects at least 99.5% of the YLF laser and transmits more than 90% of the visible light; PD: photodiode; He-Ne: He-Ne laser for alignment; M1: aluminum coated mirror; NF: notch filter; L1: laser lens; L2: achromatic lens.

al., 2001] and to 29 GPa and 920 K by wire heating [Shen *et al.*, 2004]. These studies provide important information on the physical properties of Fe, such as compressional and shear wave velocities and shear modulus under high pressures. The intensity ratio of phonon creation to phonon annihilation provides an independent source of temperature. Therefore, the application of NRIXS with the LHDAC would, for the first time, provide an absolute temperature measurement of the laser-heated sample and hence give independent verification of the reliability of the spectroradiometric method. Moreover, important physical properties of planetary materials such as magnetic, elastic, thermodynamic, and vibrational properties under simulta-

neous high pressure and temperature conditions could then be explored with both NRIXS and LHDAC techniques.

2. Experiments

[5] We have built a double-sided laser heating system at sector 3 of the Advanced Photon Source (APS), Argonne National Laboratory (ANL) for NRIXS and synchrotron Mössbauer spectroscopy (SMS) studies of materials under high pressures and high temperatures (Figure 1). A Nd:YLF laser, operating in continuous donut mode (TEM₀₁), was used to heat a metallic sample of ⁵⁷Fe (>96% enrichment) from both sides of a DAC [Shen *et al.*, 2001]. Diamonds with a flat culet of 400 μm were used to pre-indent a beryllium gasket to a thickness of 30 μm . A hole of 150 μm diameter was drilled in the indented area and filled with a sandwich configuration of Fe sample and dried NaCl as the thermal insulator and pressure medium on both sides of the sample. The use of beryllium gasket insured low absorption of the Fe K-fluorescence radiation. Small ruby chips were used as an internal pressure calibrant.

[6] During the experiments, the diameter of the laser beam at the sample position was about 40 μm . After the system spectral response was calibrated using a standard tungsten ribbon lamp with known radiance, greybody temperatures were determined by fitting the thermal radiation spectrum between 670 nm and 830 nm to the Planck radiation function [Heinz and Jeanloz, 1987; Heinz *et al.*, 1991; Shen *et al.*, 2001]. Multiple temperature measurements and temperatures across the laser-heated spot resulted in a temperature uncertainty (1σ) between 60 K and 120 K. The detailed designs and experimental procedures of the laser-heating system are similar to a system installed at GSECARS of the APS [Shen *et al.*, 2001]. A back-illuminated CCD enabled us to measure temperatures above 1000 K using the spectroradiometric method whereas the temperature determined by detailed balance principle is not limited by the intensity of the thermal radiation below 1000 K [Shen *et al.*, 2004].

[7] The NRIXS experiments were conducted using a high-resolution monochromator with 1 meV energy bandwidth. Energy spectra were obtained by tuning the x-ray energy (± 70 meV) around the nuclear transition energy of 14.4125 keV and collecting the Fe K-fluorescence radiation that was emitted with time delay relative to the incident x-ray pulses. The fluorescence radiation was collected by three avalanche photodiode detectors (APD), and the fourth APD at the end was used to record synchrotron Mössbauer spectra (Figure 1). The diameter of the focused x-ray beam was less than 10 μm (FWHM); the small beam size insured that the signal from the sample was measured only within the laser-heated spot of 40 μm . At present the counting time for each spectrum is 45 minutes to an hour, and 10–15 spectra were collected at the same pressure and temperature conditions and added.

3. Absolute Temperature Measurements Based on Detailed Balance Principle

[8] We have measured temperatures of the laser-heated sample by two different methods, spectroradiometry [Heinz and Jeanloz, 1987; Shen *et al.*, 2001] and temperature-dependent intensity asymmetry of the energy spectra based

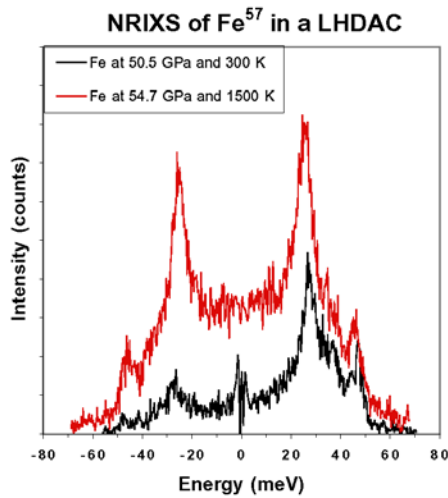


Figure 2. Representative energy spectra of hcp-Fe at 50.5 (± 2.5) GPa and 300 K (black curve) and 54.1 (± 3.2) GPa and 1500 K (± 100) (red curve) after the elastic peak at zero energy was removed. At present the counting time for each spectrum is approximately 10 hours. Negative/positive energies indicate net phonon annihilation/creation. At 300 K (black curve) the probability of phonon annihilation is clearly smaller than that for phonon creation. This imbalance is reduced at higher temperature (red curve) because phonon creation and annihilation probabilities grow equally fast with temperature. The asymmetry of these spectra was used to determine the average absolute temperature of the laser-heated sample.

on the detailed balance principle. Here NRIXS spectra of Fe were measured up to 58 GPa and 1700 K, and we used the detailed balance principle to determine the average temperature of the laser-heated sample. In Figure 2, the side band at positive energies represents phonon creation, whereas the side band at negative energy arises from phonon annihilation. The NRIXS spectra are noticeably asymmetric at 300 K; this intensity imbalance in phonon annihilation and phonon creation is reduced with increasing temperature due to the rising thermal population of the phonon levels, which adds equal portions to creation and annihilation parts. The asymmetry of the NRIXS spectra is independent of sample properties other than temperature and is given by the Boltzmann factor, $\exp[-E/k_B T]$ with the Boltzmann constant k_B , temperature T , and energy E . Therefore, the intensity ratio is given by

$$\frac{I(E)}{I(-E)} = e^{\frac{E}{k_B T}} \quad (1)$$

where $I(E)$ is the intensity of the phonon creation and $I(-E)$ is the phonon annihilation. Each pair of measured intensities $I(\pm E)$, where $E = 0$ corresponds to the nuclear transition energy of 14.4125 keV (the band width is 4.66 neV), gives a temperature value. The average temperature of the laser-heated sample is then determined by integrating all energy pairs from the energy range of 5 meV to 70 meV using the following equation:

$$\int I(E)dE = \int e^{\frac{E}{k_B T}} I(-E)dE \quad (2)$$

The average so determined gives the sample temperature within the statistical accuracy of the spectra, which is 5–10% in our case. When the sample was heated evenly on both sides, these temperatures showed very good agreement with temperatures obtained from fits of the measured thermal radiation spectra to Planck radiation function up to 1700 K (Figure 3). For example, at 54.7 (± 2.7) GPa a temperature of 1500 (± 100) K was determined from the detailed balance of the energy spectra, while the temperature averaged from multiple radiative measurements across the laser-heated spot over a period comparable to the data collection time was 1450 (± 120) K (Figure 3).

[9] Error analyses of the temperature determination based on the principle of the detailed balance show that the uncertainty in temperature increases at very low temperature where the intensity of the phonon annihilation is too weak and at ultrahigh temperature where the intensity ratio is almost equal to 1 [Shen *et al.*, 2004]. However, the counting rate is also high at higher temperatures which, in turn, would improve the statistical accuracy.

4. Discussion and Conclusion

[10] The spectroradiometric method for temperature measurement in the LHDAC has been widely used to study planetary materials, but the accuracy of obtained temperature values has been debated [Heinz and Jeanloz, 1987]. Here we have merged LHDAC and NRIXS techniques to obtain primary high-temperature scale and to explore particular physical properties of deep-Earth materials. Our study of hot hcp-Fe compared temperature measurements using the detailed balance of the energy spectra and the analyses of radiative emission spectra fitted to the Planck radiation law. Our results indicate that these temperatures

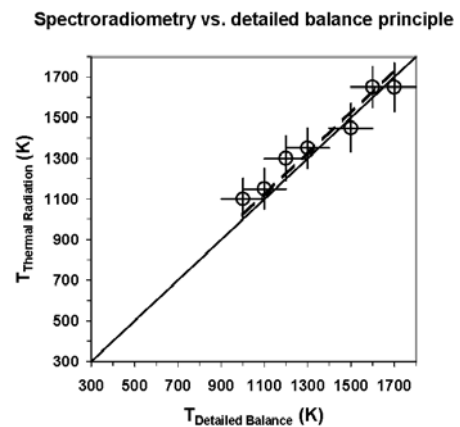


Figure 3. Comparison of the temperatures determined from the detailed balance principle and the spectroradiometric method. The dotted line is the linear regression fit to the data whereas the black line represents one-to-one reference line. The temperature from spectroradiometric method is slightly higher than that obtained by the detailed balance principle because the surface temperature (spectroradiometry) was expected to be higher than the average temperature in the heated area (detailed balance principle). These temperatures were collected from the heated hcp-Fe sample at 43 GPa to 60 GPa.

are in very good agreement with each other within statistical errors up to 1700 K. The data independently confirm the validity of temperatures determined from the Planck radiation law in LHDAC experiments. However, temperature-dependent spectral emissivity should be taken into account in the spectroradiometric method at higher temperatures where the spectral emissivity may be affected by high temperature [Heinz *et al.*, 1991; Shen *et al.*, 2001].

[11] The intensity ratios of the anti-Stokes/Stokes excitation pairs of the Raman spectra have been used to determine average temperature in a LHDAC based on the principle of the detailed balance [Lin *et al.*, 2004; Santoro *et al.*, 2004]. The intensity ratio of anti-Stokes to Stokes is given by

$$\frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = \left[\frac{\nu_0 + \Delta\nu_i(\text{T})}{\nu_0 - \Delta\nu_i(\text{T})} \right]^4 f(\nu) \exp\left[-\frac{hc\Delta\nu_i(\text{T})}{k_B T}\right] \quad (3)$$

where c is the speed of light, ν_0 is the wave number of the exciting laser light, $\Delta\nu_i(\text{T})$ is the wave number of i th Raman mode (cm^{-1}), and $f(\nu)$ is the spectral response of the system [Long, 1977]. However, the temperature effect on the cross section and the correction factor ($f(\nu)$) of the system response make it difficult to obtain absolute temperatures from the Raman spectra. On the other hand, the temperature effect on the nuclear resonant cross section is negligible, and the correction factor for the spectral response is not needed [Sturhahn, 2004]. Therefore, the imbalance (left/right ratio) of the NRIXS spectra is independent of the sample properties other than temperature itself and can provide an absolute temperature scale.

[12] The absolute temperature measurement is also very useful at temperatures below 1000 K where the spectroradiometric method is limited due to the weak thermal emission. Lattice dynamic models can be used to derive the DOS of the hot dense iron [Sturhahn *et al.*, 1995; Sturhahn, 2000, 2004] from the NRIXS energy spectra and hence the Debye sound velocity, compressional and shear wave velocities, and shear modulus can be obtained under high pressures and temperatures [Mao *et al.*, 2001]. The major lower mantle components, silicate perovskite and magnesiowüstite, contain iron, and hence, our technique is also suited to study these materials and can further advance our understanding of the Earth's lower mantle. Our study also exploited the capability of laser-heating samples in a DAC for up to half a day, advancing the application of the LHDAC technique in mineral physics research.

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