Because the average grain size of the polycrystalline CVD diamond films is comparable to the charge collection distance measured in these films, a large percentage of the charge carriers must be influenced by the grain boundaries. However, combined electron and hole mobilities for the CVD films are comparable to those measured in IIa diamonds and the dependence of the mobility and lifetime is also similar. This indicates that the mobility is not adversely affected by the grain boundaries in polycrystalline diamond films. This unexpected result along with the recent improvements in the electrical transport properties are encouraging findings in the development of diamond electronic devices. Fast, radiation-hard detectors for ionizing radiation may be among the first of such devices.

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Experimental Evidence for a New Iron Phase and Implications for Earth's Core

S. K. Saxena, G. Shen, P. Lazor

Iron is known to occur in four different crystal structural forms. One of these, the densest form (ε phase, hexagonal close-packed) is considered to have formed Earth's core. Theoretical arguments based on available high-temperature and high-pressure iron data indicate the possibility of a fifth less dense iron phase forming the core. Study of iron phase transition conducted between pressures of 20 to 100 gigapascals and 1000 to 2200 Kelvin provides an experimental confirmation of the existence of this new phase. The ε iron phase transforms to this lower density phase before melting. The new phase may form a large part of Earth's core.

Iron has been thought to occur in four solid structural states: δ (body-centered-cubic, bcc), α (bcc), γ (face-centered-cubic, fcc), and ε (hexagonal close-packed, hcp). The ε phase has been considered to constitute the bulk of the solid inner core and, with some additional light elements (sulfur, for example, or oxygen), the liquid outer core (*1*). With the availability of new experimental data (*2–11*) and theoretical considerations (*3*), this model of the core has come under scrutiny. Currently available experimental data (*2–11*) on phase equilibrium relations from static devices (techniques with in situ heating of a sample under pressure over a period of time) are displayed in Fig. 1. The phase transition boundaries α-γ, γ-ε, and α-ε meet at one point, the so-called triple point; at such pressure and temperature all three forms of iron coexist in equilibrium. Recent theoretical study on iron properties at high pressure and high temperature by Anderson (*12*) has shown that determination of the ε-γ phase transformation and the ε-γ-melt triple point are particularly crucial in understanding the state of the Earth's core. The argument is that the pressure and temperature of the triple point determines the behavior of the melting curve at high pressures. Thermodynamically, the pressure-temperature slope of the ε-γ phase equilibrium curve constrains the estimated enthalpy, entropy, and other physical properties of the ε phase, which are largely unknown. With the availability of the equilibrium data on the ε-γ phase transformation, one may assess the thermodynamic properties of the ε phase, which in turn can be used in the estimation of the properties of the iron melt.

A triple point, similar to the one shown in Fig. 1, should exist for the coexisting γ, ε, and melt. Available experimental data on the ε-γ transition appear to indicate that such a triple point would be at about 2700 K and 60 to 70 GPa. The problem is that Brown and McQueen (*13*) located a solid-solid transition at 4400 ± 300 K at a pressure of 200 ± 2 GPa. This phase transition could not be the ε-γ transition; the triple point is located at too low a pressure for this to be possible. This apparent inconsistency between the sets of data led Boehler (*15*) to conclude that a fifth iron phase should exist; Ross *et al.* (*16*) and Young and Grover (*17*) indicated that such a phase is theoretically

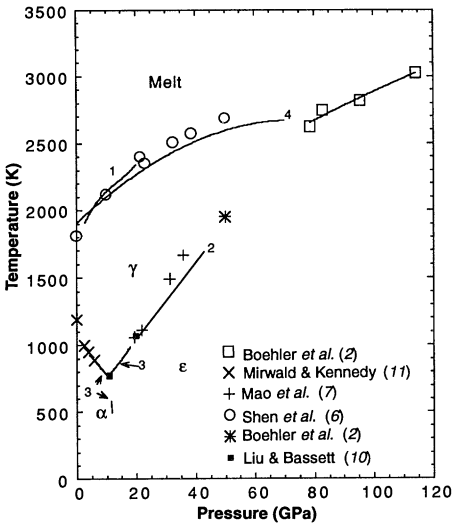

Fig. 1. Representative available experimental data on iron phase relations. Several sets of data below 10 GPa and the stability field of δ bcc phase have not been shown. The three iron phases α, γ, and ε are, respectively, the bcc (body-centered-cubic), fcc (face-centered-cubic), and hcp (hexagonal close-packed). Curve labeled 1 is from Liu and Bassett (*10*), 2 is from Boehler (*15*), 3 is from Bundy (*9*), and 4 is from Boehler *et al.* (*2*).

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possible. The existence of this phase is supposed to solve two problems; first it would explain the phase transformation recorded by Brown and McQueen (*13*) in their shock-wave studies and second, by creating a third triple point (ε-γ-melt), it would allow the slope of the melting curve to fit the geophysical data. In this report, we provide experimental evidence for the existence of a new phase. However, its pressure-temperature field of stability is quite different from the one that was expected, thus the data imply that there may yet be a sixth undiscovered phase. At present in absence of any structural information on the new phase, we simply call it as the fifth or the β-iron phase.

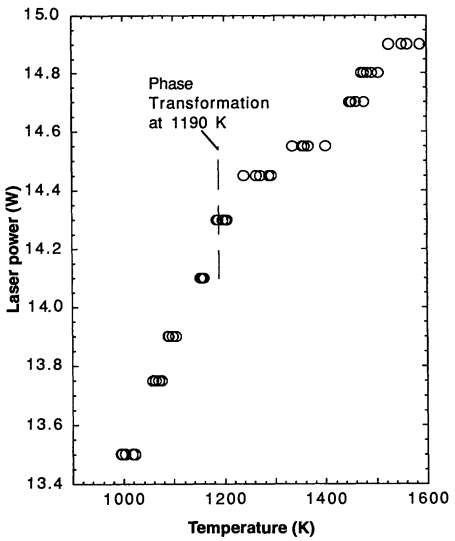

Fig. 2. Technique of determining the phase transformation using laser heating. The phase transformation of bcc-iron to fcc-iron takes place at 1190 K at 1 atm which is the same as the temperature determined by calorimetry.

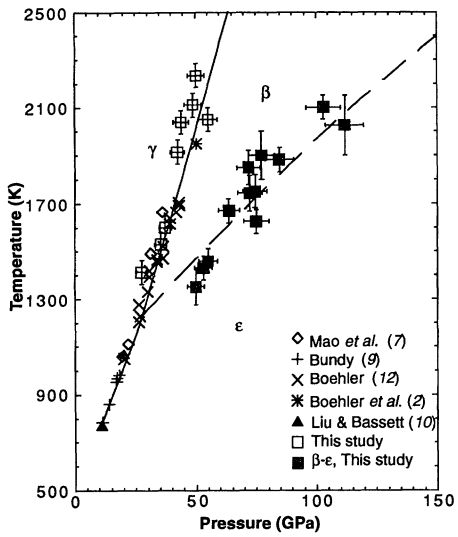

Fig. 3. Our experimental data on iron phase relations shown with error bars (*14*). The stability field of the β phase is bounded by the β-γ-ε triple point, and β-γ and β-ε transition curves. The experimental data can only show that a phase transformation has occurred. The straight-line fits of the γ-ε or the γ-β data are our interpretations. The β-γ data have been fitted by excluding the Brown and McQueen (*13*) point.

The laser heating system we used is similar to that developed by Boehler *et al.* (*2*). A Nd:YAG laser (Coherent) operating in a continuous wave TEMoo mode at a wavelength of 1064 nm was used for heating (*18*). The laser provides maximally 35 W of vertically polarized light with a feedback controlled stability better than 0.5% peak-to-peak. We used the megabar diamond anvil cell developed by Mao and Bell (*20*) for our experiments. We used standard Drukker type IA beveled diamond anvils with flat culet faces 0.30 mm in diameter. For the pressure determination the calibrated pressure shift of ruby R1 fluorescent line was used (*19*). We determined the occurrence of a phase transformation by plotting the laser power against temperature. At the temperature of phase transformation there is a distinct change in slope, as shown in Fig. 2.

The first set of data in Fig. 3 concerns the phase transformation of γ (fcc) phase to the new phase β (formerly the γ phase was considered to have directly changed to ε). Our data compares well with those of Mao *et al.* (*7*) (Fig. 3) and is only slightly at variance with that of Boehler *et al.* (*2*). The second set of data is for the β-ε transformation. As there are substantial uncertainties in the measured pressures and temperatures, it is difficult to locate the triple points accurately. The γ-β-melt point lies at 60 to 70 GPa and 2700 K (see Fig. 1); the data from Boehler *et al.* (*2*) and our data agree well in this regard. The experiments show only a phase transformation. The separation of the data between γ and the transformed phase (either β or ε) is our interpretation.

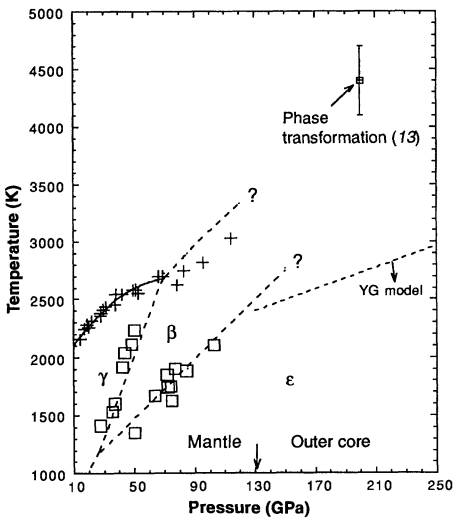

Fig. 4. Our proposed phase relations are reviewed along with data on melting [crosses (*2*)] and Brown and McQueen's (*13*) data on the phase transformation. The slope of the melting curve is not large enough to fit to the melting datum of Brown and McQueen (*13*), which lies at 5500 K and 240 GPa.

If the β-ε boundary is the same type of phase transformation as recorded by Brown and McQueen (*13*), then the change of slope of the boundary must be large to include the datum at 200 GPa and 4400 K along with the other data (see Figs. 1 and 4). We thus fit the data excluding this point. This regressed curve intersects the γ-β boundary at approximately 1230 K and 28 GPa. At high pressure, such a curve does not pass through the Brown-McQueen datum and continue with a small slope into the conditions appropriate for the core as shown in Fig. 4. The figure is schematic and is based on purely topologic considerations of the forms of the melting and phase transition boundaries as constrained by the available data.

Is there a sixth phase as originally suggested by Boehler (*15*), in addition to a fifth polymorph β, to explain the melting behavior at high pressures? From a comparison of our melting data with those of Boehler's (*2*) (see Fig. 1), it is possible that the melting temperatures may be lower at the most by 100 K. If the melting curve for the β phase (Fig. 4) continues with approximately the same slope, it could not possibly fit the melting transition found by Brown and McQueen (*13*). Boehler (*3*) considered that the shock-wave experiments may not represent equilibrium and that the temperature of the phase transition could be lower than 4400 K and that of melting lower than 5500 K and substantially lower than what Bass *et al.* (*14*) found. Additional static experiments are required to explain the shock-wave data.

The stability of the phase β at the pressures and temperatures of the outer core as shown schematically in Fig. 4 rather than the ε phase may solve certain problems related to the core density and thermal gradient. If the outer core were to form from a melt of the high-density ε phase, it would require a significant quantity of a light substance (for example, O or S) to bring the melting temperature down to a value consistent with the geophysical data. The schematic melting curve for β crosses the core-mantle boundary at about 3300 K. Boehler (*3*) suggested that the temperature of the silicate mantle at the core-mantle boundary should be between 2550 and 2750 K. The difference between the two temperatures could be reduced by mixing β with impurities or perhaps a thermal model could be found that requires no mixing at all.

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18. The spectrograph collects the radiation from an area of 3 μm in diameter of the sample through a pinhole with 50 μm in diameter. The temperature gradient over this area is only a few degrees. The error bars in Fig. 2 reflect the laser power fluctuation (root mean square is less than <0.5%). We followed the method suggested by Boehler *et al.* (*2*) in using a ruby crystal on the top of the sample as the isolator. The use of crystals eliminates the possibility of any significant reaction with the sample. In particular at the subsolidus temperature range of our study, reaction between the iron and the ruby was not a problem. A circular area with diameter of 3 μm was sampled by the spectrograph to get one pressure value; this method reduces errors in pressure determination resulting from the presence of a pressure gradient in the chamber. The pressure was determined at room temperature. Following the discussion by D. L. Heinz [*Geophys. Res. Lett.* **17**, 1161 (1990)], we added 7% to the observed value to account for the thermal pressure. Before measurement, we heated a spot with the laser to relax the sample assemblage mechanically The pressure usually dropped by up to 16% of the initial unrelaxed value. The pressure drop was almost linear and could be stabilized by repeated heating. The errors in pressure shown in Fig. 2 are based on a value of 7% and thus accounts for not only point to point variation within the heated area of the sample (within 1%) and any misjudgment of the thermal pressure
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21. Although our study was not concerned specifically with melting, we used melting data in summarizing the iron phase relations. Boehler *et al.* (*2*) found that iron melts at substantially lower pressures than did Williams *et al.* (*4*). This has led to considerable arguments over the use of solid pressure medium and the possibility of reaction between the solid and iron. However, Jeanloz (*1*) did not find any reaction in his studies at least to a pressure of 40 GPa. The melting data of Shen *et al.* (*6*), Boehler *et al.* (*2*), and Liu and Bassett (*10*) do match well and, with increasing temperature, begin to deviate systematically from the data of Williams *et al.* (*4*). Therefore, we have adopted the data from Boehler *et al.* (*2*).
22. We thank R. Boehler, Y. Fei, and H. K. Mao who helped us in establishing our laboratory and sharing their experience with us. Discussions with A. Belonoshko and O. Anderson were useful. The work has been supported financially by grants from the Swedish Natural Science Research Council and Wallenberg's Foundation.

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Net Exchange of CO_2 in a Mid-Latitude Forest

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The eddy correlation method was used to measure the net ecosystem exchange of carbon dioxide continuously from April 1990 to December 1991 in a deciduous forest in central Massachusetts. The annual net uptake was 3.7 ± 0.7 metric tons of carbon per hectare per year. Ecosystem respiration, calculated from the relation between nighttime exchange and soil temperature, was 7.4 metric tons of carbon per hectare per year, implying gross ecosystem production of 11.1 metric tons of carbon per hectare per year. The observed rate of accumulation of carbon reflects recovery from agricultural development in the 1800s. Carbon uptake rates were notably larger than those assumed for temperate forests in global carbon studies. Carbon storage in temperate forests can play an important role in determining future concentrations of atmospheric carbon dioxide.

Combustion of fossil fuel releases ~5.5 Gt of carbon per year (1 Gt = 10^9 metric tons) to the atmosphere (*1*), with an additional 1 to 2 Gt $year^{-1}$ released from tropical deforestation (*2*, *3*). About 2 Gt $year^{-1}$ is removed by the ocean (*4*, *5*) and 3 Gt $year^{-1}$ accumulates in the atmosphere (*6*). The balance, 1 to 2 Gt $year^{-1}$, is often presumed (*6*, *7*) to be stored by aggrading temperate forests. However, available estimates (*3*, *8*) indicate that the rates of net carbon uptake by temperate forests are insufficient to balance the global carbon budget.

Mean rates for carbon uptake by aggrading temperate forests have been estimated as 2.5 metric tons per hectare per year for 50 years after disturbance, near zero at longer times (*3*). Early models for global rates of carbon uptake assumed that temperate forests accrete carbon linearly with time during succession (*3*), with equilibrium carbon stocks estimated on the basis of allometric relations derived from a small number of destructive harvests (*9–11*) and with limited information on belowground components (*10*). Estimates of rates for carbon uptake by forests can be significantly refined if the eddy correlation technique is used to determine the net ecosystem flux (*12*), for time scales from hours to years. This method provides a direct measurement of annual net uptake as well as information on underlying ecosystem processes. However, eddy correlation studies have not been carried out for periods long enough to define seasonal or annual carbon exchange in forests (*13*).

In this report we present nearly continuous measurements of net ecosystem exchange (NEE) for CO_2 for 2 years in a regenerating temperate forest using the eddy correlation method. We determined hourly, daily, and seasonal net fluxes for the ecosystem for 1990 and 1991. Our study site was located at Harvard Forest, Petersham, Massachusetts (42.54°N, 72.18°W; elevation, 340 m), in a 50- to 70-year-old mixed deciduous forest (red oak, red maple, and white and red pine, with scattered individuals of yellow and white birch, beech, ash, sugar maple, and hemlock). The terrain was moderately hilly, ~95% forested, with the nearest paved roads >1 km away and small towns >10 km away.

We instrumented a tower to measure the exchange of CO_2 by eddy correlation at an altitude of 30 m, 6 m above the canopy (*14*). We computed the vertical flux from the covariance of fluctuations of vertical wind speed with CO_2 concentrations, averaged over 30 min (*14*, *15*), with special consideration of nighttime data (*16*). We obtained companion measurements of CO_2 concentrations sequentially (two cycles per hour) at 29, 24, 18, 12, 6, 3, 1, and 0.05 m, using an independent gas analyzer. The net exchange of CO_2 between the atmosphere and the vegetation plus the soil, the NEE (in kilograms of carbon per hectare per hour) is defined by

$$\mathrm{NEE} \equiv \phi_{soil} + \int_0^{30\ \mathrm{m}} (R_a - P)dz \qquad (1a)$$

where P is canopy photosynthesis, ϕ_{soil} is soil flux, and R_a is aboveground respiration. Our measurements of the eddy corre-

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