Pressure-Induced Structural Phase Transitions in Solid Xenon

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Pressure-induced structural phase transitions have been observed in solid xenon by high-pressure x-ray diffraction methods up to 137 GPa (1.37 Mbar). The face-centered cubic structure is unstable above 14 GPa and transforms to an intermediate, close-packed phase. Above 75 GPa a further transition takes place to the hexagonal close-packed structure which remains stable to at least 137 GPa. At this pressure, where $V=10.5\pm0.2$ cm^3/mol ($V/V_{01}=0.30$), there is no evidence for band-gap closure.

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The relative stability of the close-packed structures of rare-gas solids has been of experimental and theoretical interest for many decades.[1] The face-centered cubic (fcc) structure has been observed over all accessible ranges of temperature and pressure for all the rare-gas solids (other than helium and metastable, low-temperature condensates) in distinct disagreement with the predictions of theoretical models based on two-body interactions. Xenon, in particular, has been the focus of experimental investigation because its insulator-to-metal transition is predicted to be within the range of static techniques.[2,3] As a result, a number of optical[4,5] and x-ray diffraction studies[6-9] have already been carried out at high pressure. The possibility of a transition to the hexagonal close-packed (hcp) structure in xenon was first mooted after augmented-plane-wave (APW) and linear muffin-tin-orbital band-structure calculations suggested that helium would transform to the hcp structure under compression.[3] More recent total-energy calculations for compressed argon[10] suggest that the fcc phase might transform to the hcp phase prior to metallization and subsequently to a body-centered cubic (bcc) phase. It was further suggested that this transformation sequence may be exhibited by the heavy rare-gas solids in general, but no experimental support for the hypothesis was available.

In this Letter we report the first observation of a structural phase transition in a heavy rare-gas solid. Structural data have been obtained for solid xenon to 137 GPa; these measurements represent the highest-pressure diffraction data obtained so far from a condensed gas. Solid xenon is unstable in the fcc structure above 14 GPa at room temperature. The hcp stability field begins above $\simeq$75 GPa. The transition from cubic to hexagonal close packing is not direct, and appears to progress through an intermediate, close-packed structure. No visible change in the optical absorption accompanies these structural changes and at the maximum pressure of the present study (137 GPa) there is no evidence for closure of the band gap (metallization).

In this study, xenon was loaded into a diamond-anvil cell designed for generation of pressures in the 100-GPa range according to procedures described elsewhere.[11] The diffraction measurements were performed at the National Synchrotron Light Source by energy-dispersive scattering of a white x-ray beam. The diffracted x-ray beam was collected with a solid-state, Si(Li) detector. The small scattering volume resulting from the small sample thickness at the highest pressure ($\leq 10\,\mu$m), coupled with the fine collimation required to probe the sample, made the synchrotron source indispensable in the experiment. Pressures were measured *in situ* by x-ray-induced ruby fluorescence which obviated the need for an internal pressure standard. Pressures were calculated from the quasihydrostatic calibration of the wavelength shift of the R_1 line.[12] A powder refinement program[13] was used to calculate diffracted intensities for particular structure types.

Powder diffraction patterns for solid xenon as a function of pressure are shown in Fig. 1. The (111) and (200) lines of the fcc phase [Fig. 1(a)] split into a number of closely spaced diffraction peaks beginning at $\simeq$14 GPa. The initial appearance of the new phase (Xe II) is characterized by a distinct broadening of the (111)-(200) region of the fcc pattern. The (311) and (222) reflections of the fcc pattern merge to form a single peak in Xe II. A counting time of 2000 s was required in order to resolve adequately the diffraction peaks of Xe II at 26.6 GPa [Fig. 1(b)]. The transition back to the fcc structure (Xe I) is reversible and was observed by our traversing the x-ray beam down the slight pressure gradient to a low-pressure region of the sample. The forward transition seemed sluggish, however, and occurred over a large pressure interval ($\simeq$10 GPa). A significant factor in detection of this phase change was that the incident beam size could be reduced to the order of 10 μm to collect diffraction spectra from several positions within the small sample volume. The same diffraction pattern was observed from all points of the sample and the broadening of the (111) reflection could, therefore, not be attributed to nonhydrostatic or strong preferred-orientation effects.

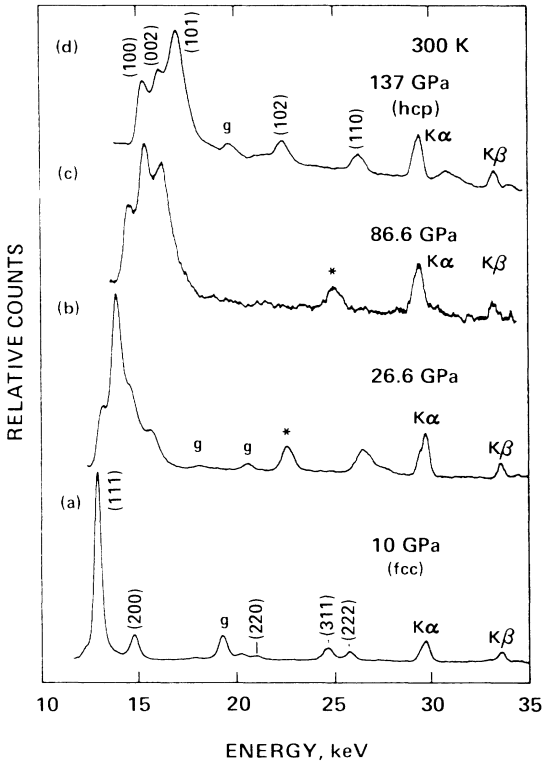

FIG. 1. Representative energy-dispersive x-ray diffraction spectra for solid xenon showing the transitions from Xe I (fcc) → Xe II → Xe III (hcp) with increasing pressure. (a), (b) $E^*d = 38.643(17)$ keV-Å; (c),(d) $E^*d = 38.317(7)$ keV-Å. The Compton background has been subtracted. $K\alpha$ and $K\beta$ are xenon fluorescence lines; g is weak diffraction from gasket (iron); the asterisks designate reflections considered diagnostic of close packing.

The structure of Xe II appears to be close-packed on the basis of the continuity of reflections marked with an asterisk in Figs. 1(b) and 1(c) with the (110) reflection in the hcp pattern [Fig. 1(d)] that is diagnostic of a close-packed stacking of layers. This reflection originates from the close-packed plane perpendicular to [00.1] in hcp. The diffraction pattern shown in Fig. 1(b) cannot be decomposed into a sum of fcc and hcp contributions and a polymorphic transition to the body-centered cubic structure is also excluded. An alternative explanation for the observed diffraction pattern is that fcc xenon undergoes a polytypic transition that results in a large-period, cubic-hexagonal layered structure of the type found in close-packed metal[14] and in recent molecular-dynamics simulations of the fcc → hcp transition[15] with compression along the [100] direction. The transformation mechanism may be similar to the temperature-induced fcc-hcp transition in solid H_2 and D_2, where the existence of intermediate close-packed structures was also postulated.[16] In addition, the apparent sluggishness of the transition to Xe II may be indicative of a martensitic transformation mechanism[17]: A pressure-induced shear of the close-packed layers relative to one another could be responsible for the formation of intermediate structure(s) with mixed cubic-hexagonal character.

TABLE I. Energy-dispersive powder data for solid xenon (Xe II) at 26.6 GPa. *a* and *b* are overlapped peaks.

E (keV)	d_{obs} (Å)	I/I_1	FWHM[a] (keV)	Notes
13.132	2.943	29	0.53	
13.884	2.783	100	0.60	
14.600	2.647	92	0.97	
15.698	2.462	42	0.97	
18.151	2.129	2	0.69	ϵ-Fe
20.598	1.876	4	0.56	ϵ-Fe
22.527	1.715	13	0.56	*a*[b]
22.872	1.690	4	0.49	*a*
26.420	1.463	20	0.74	*b*
26.865	1.438	4	0.54	*b*
27.522	1.404	9	1.02	*b*

[a]The error in fitted peak position is a few electronvolts, but is assumed to be proportional to peak width.

[b]Reflection considered diagnostic of close packing.

Several structure assignments were tried for Xe II based on the known intermediates of the trivalent rare-earth metals.[18,19] Despite an overall similarity, the *d* values of the Xe-II powder pattern are not matched by either the dhcp structure type (four-layer repeat, *ABAC*...), thcp (six-layer repeat, *ABCACB*...), nor Sm type (nine-layer repeat, *ABCBCACAB*...). The intensities of the observed reflections cannot be used reliably in structure determinations because of the uncertainty in degree or preferred orientation of the sample. The large stability field of Xe II does suggest, however, that it is a stable intermediate phase in the fcc → hcp sequence. The pattern of four overlapped peaks is broadly similar for all the powder diffraction spectra collected between 21 and 75 GPa, although poorly resolved in some cases. Table I lists the *d* values and relative intensities measured for this phase at 26.6 GPa. Further studies at higher resolution and with larger sample volumes will be needed in order to work out the structure in detail and to determine the effects (if any) of stacking faults.

Previous x-ray diffraction investigations to 55 (Ref. 6), 32 (Ref. 7), and 23 GPa (Ref. 8) with conventional film techniques reported no observation of a phase change up to the maximum pressures in each experiment. In some of these studies, however, problems in the analysis of the data above $\simeq$12 GPa were reported,[7,8] including systematic discrepancies in line positions, missing reflections and nonuniformity of exposure. It seems likely that these effects were associated with the transition observed in this study at 14 GPa were the first occurrence of broadening in the (111)-(200) region was observed in the energy-dispersive patterns. In view of

the overall similarity of the diffraction pattern of the intermediate phase to that of Xe I and the broad pressure range of the phase change, it is perhaps not surprising that the transition was not identified in these earlier studies. In fact, if the most intense line of the Xe-II diffraction pattern is indexed as fcc(111) and used to calculate the cell volume, then no discontinuity in volume occurs in the equation of state from fcc to hcp. There was no evidence for the transition in a diffraction study to 11 GPa at 85 K (Ref. 9).

Above $\simeq$75 GPa a further change was observed in the diffraction pattern [Fig. 1(c)] involving a shift in the splitting and intensities of the quadruplet. Above 80 GPa the splittings appeared stable though not well resolved. At 137 GPa, the pattern can be indexed as hexagonal close packed [Fig. 1(d) and Table II]. Because of anomalous splitting in this second transition region [Fig. 1(c)], low resolution, and the limited coverage in pressure, it is not possible to determine conclusively whether there is further intermediate close-packed phase of xenon, existing over a narrow pressure interval, or whether c/a is changing rapidly prior to conversion to the hcp phase (Xe III). The thickness of the sample had been significantly reduced at the maximum pressure and an integration time of 9100 s was required to produce the diffraction pattern shown in Fig. 1(d).

The molar volume as a function of pressure is plotted in Fig. 2. For the hcp phase, the volumes were calculated from the (100), (002), and (101) reflections. The measured c/a ratio (1.64 ± 0.02) is very close to ideal for the hcp structure and shows no systematic dependence on the pressure. [Errors are propagated from a least-squares fit to the d values weighted (arbitrarily) by one-half the FWHM of each diffraction peak.] Time constraints prevented long exposures at each pressure increment and, consequently, weak lines are not well resolved. Figure 2 also shows the equation of state from APW calculations for the fcc phase. No band-structure calculations have been performed for other structures, but it is worth noting that the measured volume of the hcp phase is close to that predicted theoretically for the fcc phase well above its observed stability field.

Stacking-fault defects due to trace impurities can stabilize metastable phases in rare-gas solids but are not considered likely explanations for the formation of the intermediate structure in these experiments since such defects are known to form near the freezing (melting) points of rare-gas solids at low temperature.[1] In the present study the apparatus was thoroughly flushed before loading and the fcc phase (not hcp) formed at the room-temperature freezing pressure. Some preferred orientation was present, as can be seen by the deviation from the ideal (111)–(200) intensity ratio at low pressure [Fig. 1(a)]. Furthermore, the Xe-I–Xe-II transition was reproducible and many crystallites must have contributed to the observed powder pattern.

Finally, it is worth noting that the molar volume measured at 137 GPa is 10.5(2) cm^3/mol ($V/V_{01}=0.30$, where V_{01} is the zero-pressure, low-temperature volume for the solid[2]), and is very close to the Herzfeld metallization limit for Xe (10.2 cm^3/mol). The present results

TABLE II. Structural data for hcp xenon (Xe III) at 137 GPa.

E (keV)	d_{obs} (Å)	I/I_1	FWHM[a] (keV)	hkl	d_{calc}[b] (Å)	I_{calc}	Notes
15.303	2.504	20	0.63	(100)	2.518	22	
16.085	2.382	28	0.81	(002)	2.368	26	
17.059	2.246	100	1.1	(101)	2.224	100	
19.701	1.945	11	1.0				ϵ-Fe
21.333	1.796	4	0.95				ϵ-Fe
22.402	1.710	11	0.81	(102)	1.725	18	
26.293	1.457	4	0.72	(110)	1.454	24	a[c]

[a]The error in fitted peak position is a few electronvolts, but is assumed to be proportional to peak width.

[b]Unit-cell parameters: $a=2.908(8)$ Å, $c=4.737(32)$ Å.

[c]Low value of the observed intensity is attributed to the falloff in photon flux from the bending-magnet source.

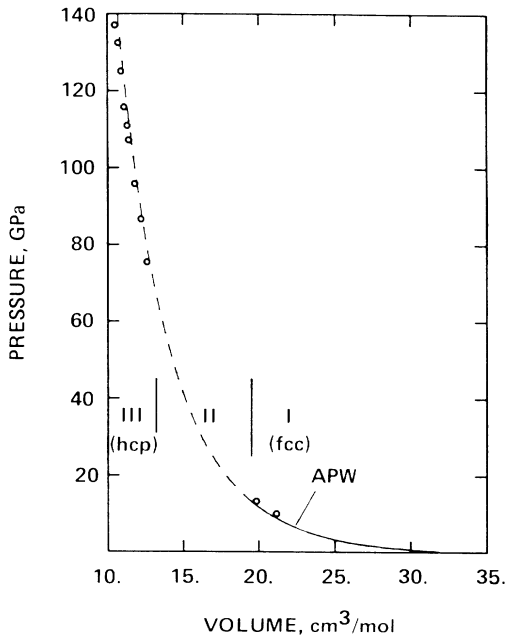

FIG. 2. Molar volume as a function of pressure for xenon to 137 GPa. The short vertical lines mark the boundaries between the close-packed modifications discussed in the text. Open circles are data from this study. No volume data are plotted for the intermediate phase. The solid line is taken from an APW electron-band structure calculation for the fcc phase of condensed xenon at $T=0$ (Ref. 2); the dashed line represents the fcc volume obtained from this calculation outside the fcc stability field. No volume discontinuity is observed within the scatter of the data.

indicate, however, that the band gap remains outside the visible region at this volume. If the fcc→ hcp transition sequence is driven by the effects of hybridization and closure of the gap, as has been suggested recently,[10] then the free energy of the phases must be sensitive to changes in the band gap above $\simeq 3$ eV. In any event, the results are likely to provide important constraints on the relative contributions from pair and many-body forces in the fcc and hcp structures (as well as related polytypes) in this fundamental class of solids.

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