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Structural transformation of compressed solid Ar: An x-ray diffraction study to 114 GPa

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Room temperature angle-dispersive x-ray diffraction measurements on solid Ar up to 114 GPa reveal evidence of a structural phase transformation after stress relaxation by laser heating. Beyond 49.6 GPa, Ar exhibits the coexistence of fcc and hcp phases with an increasing hcp/fcc ratio, similar to the observation made recently on krypton and xenon. From the present results, we estimate the fcc-to-hcp transition to be completed at 300 GPa.

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The properties of rare-gas solids at high pressure continue to attract much experimental and theoretical attention since they provide a critical test of theories of bonding of solids.[1–12] In particular, rare-gas solids are excellent candidates to study pressure-driven phase transitions. They form simple crystal structures, all of them have a fcc structure at low pressures and have an electronic charge distribution close to that of the free atoms. However, the pressures now experimentally achieved can lead to a redistribution of their electronic structure, driving profound changes in their physical and chemical properties [e.g., xenon (Xe) metallizes at 138 GPa (Ref. 13)]. Upon compression, Xe transforms martensitically from the fcc to the hcp structure between 3 and 70 GPa.[6,9] For krypton (Kr), the same transition has been reported to start at 3.2 GPa, being expected to be completed around 170 GPa.[6,9] It has been suggested that the stabilization of the hcp structure is caused by the hybridization between the s,p valence bands and the d band.[5] According to this argument, the fcc-to-hcp transition should also occur in the light rare-gases, e.g., argon (Ar), but at higher pressures. *Ab initio* calculations locate the transition for Ar near 230 GPa,[5,10] but no experimental data existed to confirm this prediction.

Here we report angle-dispersive x-ray diffraction (ADXRD) data showing evidence of the coexistence of fcc and hcp phases in Ar. As in the case of Xe and Kr, the phase coexistence is observed over a large pressure range. The onset of the hcp phase is observed at pressures as low as 49.6 GPa, but the transition is not complete at 114 GPa, the highest pressure of this study. From the analysis of the relative intensities of the (100) Bragg peak of the hcp structure and the (200) Bragg peak of the fcc structure, the fraction of hcp phase as a function of pressure has been estimated. From the present results, we estimate the fcc-to-hcp transition to be completed at 300 GPa.

The ADXRD experiments were performed at the ID27 beamline of the European Synchrotron Radiation Facility (ESRF). Monochromatic radiation ($\lambda = 0.3738$ Å) was used for ADXRD pattern collection on a Mar345 image plate detector. The x-ray beam was focused down, using Kickpatrick-Baez mirrors, to 10×10 μm^2. The diffraction images were integrated and corrected for distortions using the FIT2D software[14] to yield one-dimensional intensity versus 2θ diagrams. Indexing and refinements were performed using the POWDERCELL software.[15] The samples were compressed using a diamond-anvil cell (DAC) with tungsten (W) gaskets which had a 100-μm-diameter hole. High-purity Ar (99.999%) was loaded in the DAC at room temperature (RT) using a 0.3 GPa gas apparatus together with a 10-μm-thick iron (Fe) foil. Prior to each ADXRD pattern collection, at every studied pressure, the Fe foils were laser heated at high pressure with two 40 W Nd:YVO$_4$ lasers (TEM$_{00}$ mode, $\lambda = 1064$ nm) to above 2000 K. The temperatures of the Fe foils were determined from the thermal radiation spectra fitted to the Planck radiation law.[16] A ruby chip served as pressure sensor.[17] The pressures obtained in this way agreed with those deduced from W peaks according to its equation of state (EOS).[18] As observed in earlier studies,[19] pressure gradients are significantly reduced after laser heating of small samples in an argon pressure medium using similar cell arrangements as in the present study. This also leads to a substantial sharpening in the argon x-ray peaks.

Figure 1 shows room temperature ADXRD patterns of Ar measured at several pressures. In some of them, some W peaks are present. These peaks are easy to identify since their pressure shift is smaller than that of Ar peaks. Regarding the W peaks, we should note that they are at least six times weaker than the Ar peaks. It is known that the x-ray diffraction intensity is proportional to the squared atomic number of an element (18 for Ar and 74 for W). Then, the tail of the x-ray beam with 1% of the maximum intensity hitting the gasket will cause the observed W peaks. The radial distance from the x-ray beam to the Fe foil and the gasket was $\geqslant 10$ μm. Thus, with a beam size of 10 μm at full width at half maximum (FWHM) the observed x-ray diffraction from W can be produced.

The ADXRD pattern collected at 34.9 GPa can be indexed with the fcc structure. However, in the pattern collected at 49.6 GPa, we notice the appearance of new reflections. These new reflections were present in all the patterns we collected from 49.6 GPa to 114 GPa, and their intensities increase under pressure. In particular, the peaks observed in the spectra measured at 55 GPa around $2\theta = 9.1°$, 10.3°, and 13.1° cannot be attributed to the fcc phase of Ar or to the W gasket or the Fe heater. In fact, the measured patterns for Ar

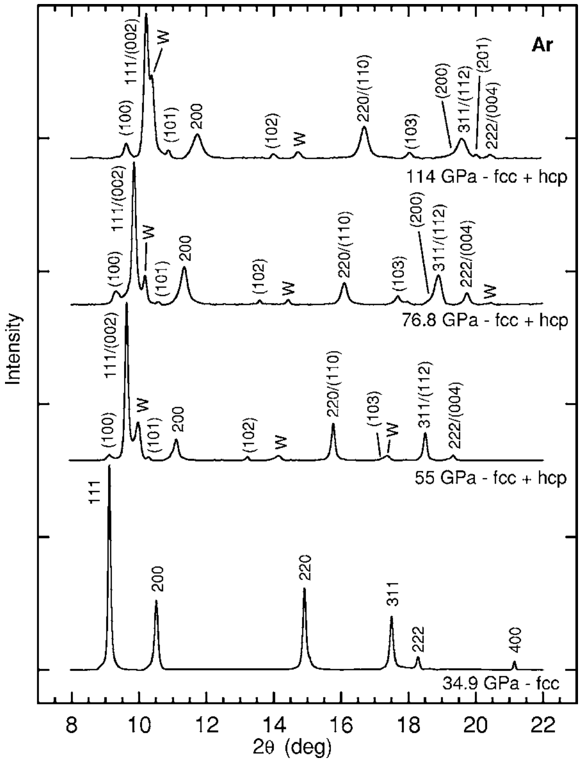

FIG. 1. RT ADXRD patterns of Ar at different pressures. Miller indices of the fcc (hcp) phase are provided. W peaks are also labeled. The background was removed.

from 49.6 GPa to 114 GPa can be indexed only on the assumption of the coexistence of a fcc phase and a hcp phase. In order to illustrate this fact more clearly, we plot in Fig. 2 the diffraction diagram of Ar at 114 GPa together with the refined profile and the individual contribution of the different phases. The results shown in Figs. 1 and 2 evidence that Ar undergoes a similar transformation as Xe and Ke under compression,[6,9] exhibiting the coexistence of the fcc and hcp phases over a wide pressure range. We would like to note here that the evolution of the diffraction patterns upon compression can be continuously tracked, giving us confidence on the fact that we are documenting a crystal structure transformation of Ar rather than a chemical reaction between Ar and Fe.

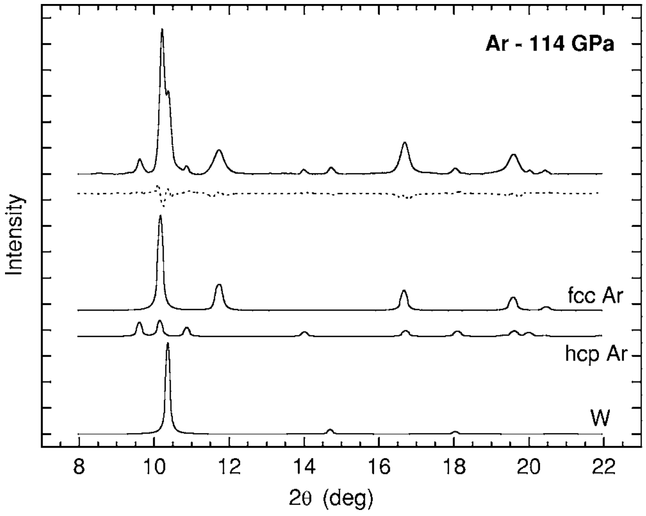

FIG. 2. ADXRD pattern of Ar at 114 GPa (upper trace). The background was removed. The difference between the measured and refined profiles (dotted line) and the individual contribution of the different phases are given.

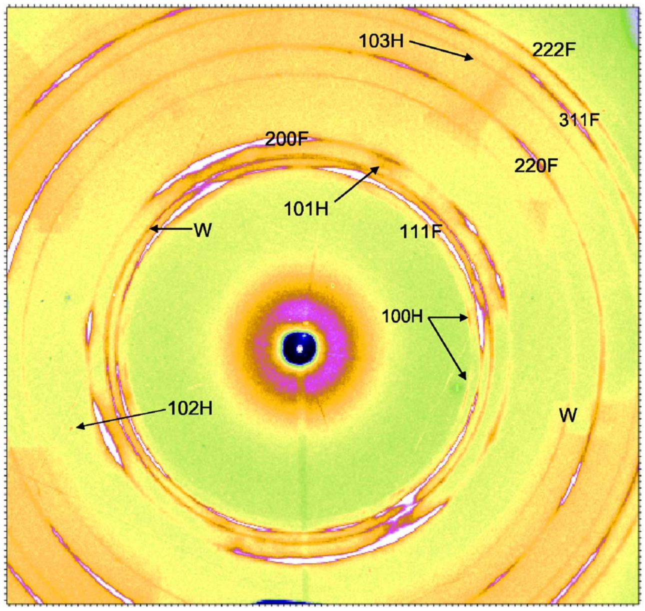

FIG. 3. (Color online) Debey-Scherrer rings as recorded on the image plate from Ar at 49.6 GPa showing the appearance of hcp rings and spots. F (H) is fcc (hcp). The rings corresponding to both phases are labeled only as fcc for simplicity. W indicates tungsten peaks.

As shown in Figs. 1 and 2, the positions of the (111), (220), (311), and (222) peaks of the fcc phase of Ar agree with those of some of the hcp peaks; e.g., (002), (110), (112), and (004). These correspondences have been observed before in Xe and Kr (Refs. 6 and 9) and are expected from disorder to stacking of close-packed layers,[9] which seems to be unavoidable in rare-gas solids.[20] In Fig. 1, it can be also seen that the intensity of the (100), (101), and (102) peaks of hcp Ar continuously increase under compression. On the other hand, the contrary effect is observed in the (200) peak of fcc Ar. Notice, that this is the only observed fcc peak not overlapping with hcp reflections. These facts indicate an increase of the amount of hcp domains present in Ar upon compression. It is important to point out here that, according to the Scherrer equation,[21] the widths of the diffraction peaks of Ar imply that the dimensions of individual domains of fcc Ar and hcp Ar are at least many nanometers.

Another demonstration of the observed extra hcp peaks of Ar is also given in Fig. 3. It shows the Debye-Scherrer diffraction rings of Ar at 49.6 GPa as recorded on the image plate. Upon compression, the ring attributed to the (002) peak of fcc becomes diffuse, while the rings attributed to hcp Ar become more intense. This kind of behavior is common for martensitic fcc-hcp transitions and seems to be related to the development of stacking disorders.[6,9,22] The fact that hcp reflections appear first as diffuse spots is also a clear indica-

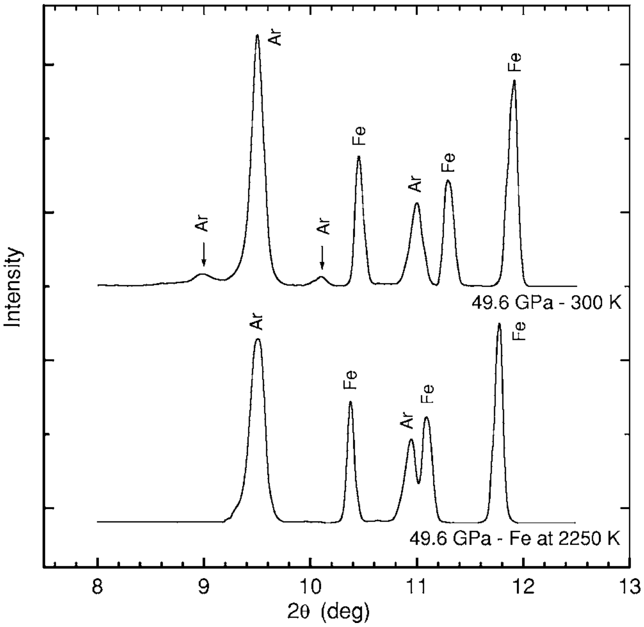

FIG. 4. ADXRD patterns taken simultaneously from Ar and Fe. The top pattern was collected at 49.6 GPa and RT. The bottom pattern was collected during laser heating (Fe at 2250 K). Ar and Fe peaks are labeled.

tion that a disorder of the stacking of the atomic layers develops in Ar under compression. It is well known that by omitting a single layer of atoms in the fcc structure an ABABAB stacking sequence (hcp) results, rather than an ABCABC stacking sequence (fcc).[6,7] From the very small energy difference between the fcc and hcp structures,[5] it is expected that thermal fluctuations could occasionally slide the position of a fcc plane to a hcp arrangement. Thus, the successive production of stacking faults under pressure seems to be fundamental for the evolution of domains of fcc Ar to hcp Ar.

Figure 4 shows two different ADXRD patterns taken simultaneously in Ar and Fe at 49.6 GPa. One of them was collected at RT. The other was collected *in situ* during laser heating, when the temperature of the Fe heater was 2250 K. A thin layer of Ar in contact with the Fe foil presumably would have been also at 2250 K, and the rest of the Ar at some elevated temperature with the exception of a thin layer in contact with the diamond anvil. In these patterns, the peaks arising from the ε phase of Fe can be distinguished from those of Ar. In Fig. 4, it can be also observed that at high temperature the two peaks inherent to hcp Ar (depicted by arrows) disappeared. This means that at high temperatures, the intergrowth of hcp and fcc phases will begin at higher pressures, confirming previous observations made in Xe and Kr.[7]

It is worth commenting here why the hcp structure was not found in previous x-ray diffraction studies in Ar.[8] One reason is the higher resolution of our x-ray measurements due to the high brilliance reached at the ESRF. Another reason is that laser heating of DAC samples has been shown to be very efficient in reducing stresses gradients build on compression,[19,23] resulting in sharper, more intense, and better resolved x-ray peaks than before the laser heating. Because of these reasons, it is not surprising that the coexistence of fcc and hcp phases was not identified in earlier experiments.

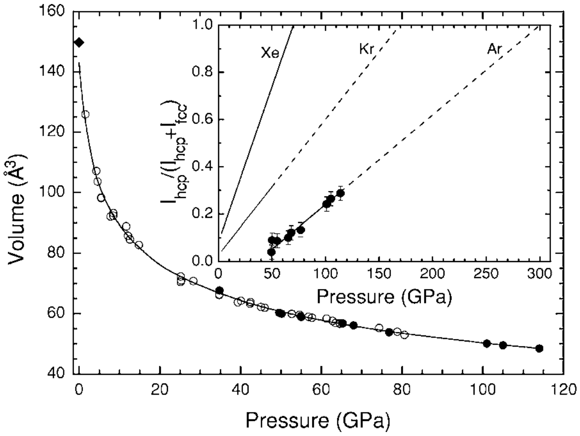

FIG. 5. Volume-pressure data of fcc Ar. Present data (●), Ref. 8 (○), Ref. 24 (◆), and fitted EOS (solid curve). Inset: relative amount of hcp Ar to fcc Ar. I_{hcp} (I_{fcc}) is the intensity of the hcp(100) [fcc(220)] peak. The error bar includes possible systematic errors from preferred orientation effects. Ar data are from this study, and Xe and Kr data are from Refs. 6 and 9. The dashed lines are extrapolations.

Figure 5 compares the pressure-volume data we obtained for fcc Ar with previous results.[8] The agreement between both experiments is excellent. The volume obtained for hcp Ar at all the pressures where this phase was present is equal to that of fcc Ar within the experimental accuracy. This is not surprising since both phases can be thought of as being polytypes of the same close-packed structure.[6,7] The close similarity between the fcc and hcp structures, which have identical first- and second-neighbor coordination shells, may explain also why the hcp Ar was not found previously. A third-order Birch-Murnaghan fit to our data yields the atomic volume, the bulk modulus, and its pressure derivative for fcc Ar: $V_0=143(11)$ Å^3, $B_0=6.5(5)$ GPa, and $B_0'=5.1(3)$, respectively. These parameters confirm the EOS reported in Ref. 8 and shows that the calculations performed by Tsuchiya *et al.* underestimate V_0 by near 10% and B_0 by at least 35%.[25] As observed in Xe and Kr,[6] we found from our data that in hcp Ar the c/a ratio remains nearly constant under pressure (close to the ideal value, 1.633); i.e., the compressibility of both axes is the same. This fact rules out the existence of any intermediate phase progressing from fcc to hcp by means of shear deformations[4] and gives additional support to the idea that fcc transforms into hcp due to the presence of stacking disorders.

The inset of Fig. 5 shows the relative fractions of hcp Ar in several samples, as estimated from the relative intensities of the fcc(200) and hcp(100) reflections (each of them relates to the main peak of its own structure), the two not-overlapping main reflections of each structure. These data show that the hcp/fcc ratio increases with pressure, reaching a value close to 0.3 at 114 GPa. A linear extrapolation of these data to higher pressure seems to be reasonable based on the behavior observed for the hcp/fcc ratio in Xe (see inset of

Fig. 5). This extrapolation gives an estimate of 300 GPa for the completion of the fcc-to-hcp transition. This value is higher than the theoretically calculated fcc-to-hcp transition pressure (230 GPa).[5] Similar differences are observed in Kr and Xe between the pressure experimentally determined for the completion of the fcc-to-hcp transition[6,9] and the theoretically calculated fcc-to-hcp transition pressure.[3,10]

As argued by McMahan,[5] a physical basis for the stabilization of the hcp structure can be drawn from the fact that the *d*-electron population contribution to the valence band increases under compression due to the *sp-d* hybridization as the gap of Ar narrows. In our case, we observed that at 114 GPa, the relative fraction of hcp Ar with respect to fcc is 0.3. This value is reached in Xe at 17 GPa (see inset of Fig. 5). At 17 GPa, the *d*-electron population in the valence band of Xe has risen by about 0.13 electrons per atom[26] from its 1 bar pressure value (10), but at the completion of the fcc-to-hcp transition (70 GPa) it has increased by 0.25 electrons per atom. If we assume than the relative fraction of hcp domains in a rare-gas solid is related to the *d*-electron population and that the fcc-to-hcp transition is completed when that population is increased by 0.25 electrons per atom, based upon a corresponding states scaling, we would expect that the fcc-to-hcp transition would be completed at 310 GPa in Ar. This value compares well with the 300 GPa estimate obtained from the linear extrapolation of the relative fraction of hcp Ar discussed above.

The relationship between pressure-induced changes in the electronic structure and the structural behavior of Ar becomes obvious from an additional observation: Around 70 GPa, we observed the disappearance of the red intrinsic luminescence observed when Ar in the DAC was irradiated by high-energy x-rays from the synchrotron source.[27] However, at 114 GPa, we found that the luminescence reappeared, but now on the blue side of the visible spectrum. This change observed in the luminescence can be only possible if the band structure of Ar is modified and thus, affecting the electronic transitions.

In summary, we detected a structural transformation of an element as simple as Ar, starting beyond 49.6 GPa after laser heating. This observation differs from previous experiments on unheated samples and seems to be related to the developing of staking disorders in fcc Ar. We found that upon compression, the fcc and hcp phases coexist from 49.6 GPa to 114 GPa. We also observed that the hcp/fcc ratio increases with pressure reaching 0.3 at 114 GPa. A similar behavior was previously observed in Xe and Kr,[6,9] suggesting that the fcc-to-hcp martensitic transition could be a common phenomenon in all rare-gas solids. From our result, we estimate an upper limit of 300 GPa for the completion of the observed transition. Further experiments are needed extending pressure beyond 114 GPa to confirm this prediction.

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