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# On the solid-solid phase diagrams of Ar-O<sub>2</sub> and Ar-N<sub>2</sub> mixtures

S. F. Ahmad, H. Kiefte, and M. J. Clouter

Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7  
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The growth of large single crystals of Ar-O<sub>2</sub> and Ar-N<sub>2</sub> alloys is reported. The crystals were formed under near or quasiequilibrium conditions and it was found that minimum solute concentrations of about 4 1/2% (N<sub>2</sub>) and 5% (O<sub>2</sub>) were required in order to produce the hcp phase. Lower concentrations resulted in the fcc phase.

## INTRODUCTION

Rare gas solids are the simplest known solids and therefore their study is of fundamental importance to the theoretical understanding of solids and lattice dynamics in general. It is well known that the rare gases, with the exception of helium, solidify in a face-centered-cubic (fcc) structure. Theory, however, predicts that solidification should be to a hexagonal-close-packed (hcp) structure, if only two-body radial forces between the molecules are considered.<sup>1</sup> To date, there is no completely satisfactory explanation for the stability of the fcc phase.<sup>2</sup>

Meyer and co-workers<sup>3-6</sup> first reported that small amounts of N<sub>2</sub>, O<sub>2</sub>, and CO in the solid stabilized hcp phase of Ar. They determined detailed solid-solid phase diagrams of these mixtures by x-ray diffraction with powder diffractometry techniques. In addition, Hägele and co-workers<sup>7</sup> have reported a measurement of birefringence in hcp Ar-2% O<sub>2</sub> single crystals. Bricheno and Venables<sup>8</sup> have conducted some vapor pressure measurements and Schubert<sup>9</sup> has observed first-order Raman scattering from polycrystalline hcp Ar and its alloys.

The present authors have performed Brillouin scattering experiments on fcc and hcp single crystals of these alloys<sup>10</sup> to investigate corresponding changes (and anomalies) in the elastic constants. In this paper, the technique of crystal growth is described and some conclusions about the phase diagrams of these alloys are reported. There appears to be some discrepancy between the present work and existing phase data.<sup>3,5,6</sup>

## APPARATUS AND TECHNIQUE

Single crystals of Ar alloys were grown by a modified Bridgman's method. The samples were produced in a cylindrical quartz cell, of 3 mm i.d. and 5 mm o.d., which was mounted vertically, in vacuum, in a modified Janis model 10-DT helium Dewar.

The cell is shown in Fig. 1 (see also Ref. 11). Two spring clips, 0.8 cm apart, were attached to the outer walls of the cell, and provided cooling via copper braids which were connected to a temperature controlled liquid helium heat exchanger in the tail section of the cryostat. The copper braids were flexible to allow rotation of the entire cell assembly. Copper rods connecting the clips and the braids were wound with 50 ohm heaters which

were used to control the temperature at the top and at the bottom of the cell. The temperature at the bottom of the cell was monitored by a calibrated GaAs diode, and the temperature gradient between the top and bottom clips was measured differentially by a copper-Constantan thermocouple. During growth, the gradient was usually kept in the 1 to 3 K/cm range. The temperature at the bottom (and top) of the cell could be maintained indefinitely to within 0.01 K utilizing Lakeshore DTC 500 cryogenic temperature controllers.

The initial gaseous mixtures (Matheson Research Grade) were prepared at room temperature and the concentration of the diatomic component was monitored by

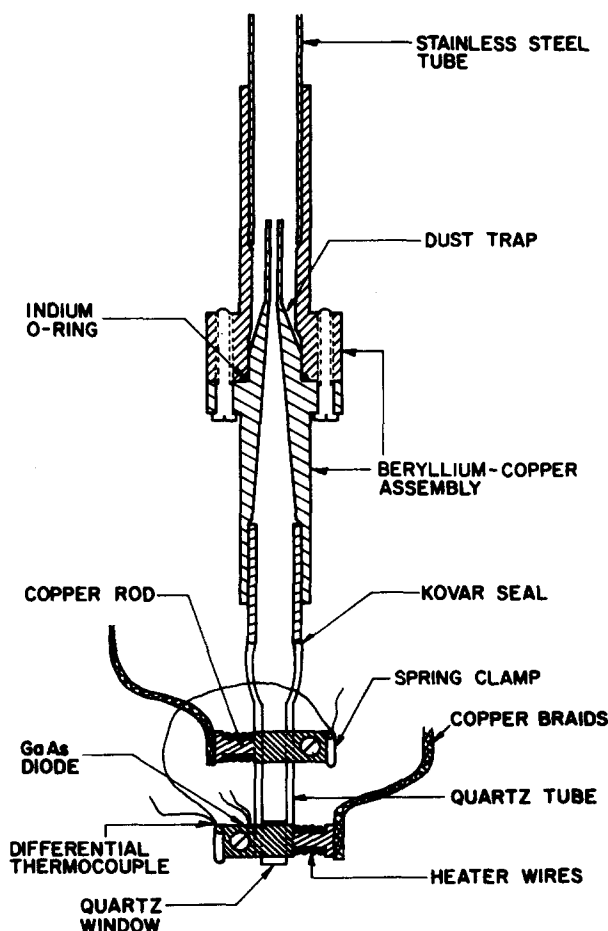


FIG. 1. Sample cell and dust collector assembly.

TABLE I. Physical data for some experimental samples of Ar-O<sub>2</sub> and Ar-N<sub>2</sub> mixtures.

Solute concentration in gas phase	Temperature at freezing point, in K	Gradient in K cm <sup>-1</sup>	Average estimated solute concentration in solid	Crystal structure
5% O <sub>2</sub>	83.3	1.2	2% O <sub>2</sub>	fcc
7½% O <sub>2</sub>	82.7	1.0	3½% O <sub>2</sub>	fcc
10% O <sub>2</sub>	81.5	1.0	6% O <sub>2</sub>	hcp
15% N <sub>2</sub>	82.5	2.0	1½% N <sub>2</sub>	fcc
22½% N <sub>2</sub>	79.3	2.0	3½% N <sub>2</sub>	fcc
30% N <sub>2</sub>	78.9	2.0	5% N <sub>2</sub>	fcc and hcp

Speedivac CG3 pressure gauges, the total initial pressure usually being about 720 mm. The free volume in the sealed gas sample system was about 1 liter. Two stages of 0.2  $\mu$ m Millipore filtering were utilized.

Liquid was first condensed in the cell by lowering the temperature to about 85 K, while a temperature difference of about 2.5 K was established between the top and bottom clips—the temperature at the top always being higher. Ideally, the freezing process should be slow enough so that equilibrium is maintained at all times; this would ensure that the solute could diffuse into the liquid and solid, and thereby eliminate possible concentration gradients. This is not realized in practice because of the slow diffusion of solute in the solid and leads to a small concentration gradient in the solid.<sup>12</sup> Nevertheless, it appeared to be important to allow the liquid to stand for several days and then to cool it very slowly to attain quasiequilibrium at all times. Crystal growth was consequently initiated by keeping the gradient constant while slowly lowering the temperature at a rate of about 0.05 to 0.1 K/h until a small seed of less than 0.5 mm height formed on the cell window. The initial freezing temperature varied with solute concentration and is given in Table I.

The seed crystal formed was then annealed for one or two days. It was then grown to a height of about 1 cm, the growth rate being about 0.05 mm/h with intermittent several hour periods of constant temperature in which no growth took place. During the vertical growth of the crystal, the solid-liquid interface was either horizontal or slightly convex towards the liquid, thus discouraging stray nucleation near the cell walls.<sup>13</sup> In total, it took to the order of ten days to grow any particular sample.

Transmission Laue x-ray diffraction photographs were taken using a Philips (MG 101) x-ray source, a lead collimator, and a Polaroid XR-7 Land diffraction camera. The Laue photographs were used to initially determine the quality of the seed and then to determine whether the final crystal was completely single or polycrystalline, fcc or hcp, and relatively free of strain. The orientation of the crystallographic axes, with respect to the laboratory frame of reference, was also determined. The orientations were calculated from, and least-squares fit to, the positions of spots on the Laue photograph using a program written for the HP 9825 electronic calculator.<sup>14</sup> This program has been generalized for any crystal symmetry and could distin-

guish between fcc and hcp structures.

The phase of the crystal was verified by two methods: (i) Crystals were always observed under crossed polaroids and any birefringence noted. hcp crystals always showed birefringence<sup>7</sup> unlike unstrained fcc crystals. (ii) Next, the crystal orientation was determined using the above mentioned program. If *all* the observed spots for a given Laue photograph could be indexed in a hcp orientation (and if there was evidence of birefringence), the crystal was assumed most probably to be hcp. Laue photographs were also taken while rotating each of the crystals up to 120° in steps of 10°. The orientation procedure was repeated independently for each such photograph and the results were checked against the angles predicted by the initial orientation of the crystal. If this stringent check were passed, then the crystal was confirmed to be single and of the hcp phase. Similarly, the absence of birefringence and the successful fcc indexing of all the spots on an initial Laue photograph indicated the crystal to be of the fcc phase, and this was also confirmed as above. It is emphasized that great care was taken to ensure that each and every spot on the Laue photographs was taken into account in the orientation procedure, and in no case was it possible to orient a crystal both as fcc and hcp.

## RESULTS

Ar-10% O<sub>2</sub> gaseous mixtures, which correspond to about 6% in the solid alloy, were found to be ideal for growing hcp crystals. Seven hcp Ar-O<sub>2</sub> single crystals, of 1 cm height, were grown. They did not exhibit any visual defects and showed birefringence under crossed polaroids. Two of the samples showed slight twinning. Many fcc single crystals were grown with 2%–4% O<sub>2</sub> (solid) concentration. Typical Laue photographs are shown in Figs. 2 and 3.

The concentration in the solid was estimated by measuring the freezing temperature and utilizing the published phase diagrams.<sup>15–17</sup> The values obtained were consistent with the initial gas mixtures. The concentration was also checked independently by comparing the intensities of O<sub>2</sub>(N<sub>2</sub>) Raman vibration lines in the Ar matrix to those in the pure O<sub>2</sub>(N<sub>2</sub>) solid.<sup>18</sup>

The growth of an Ar-N<sub>2</sub> single crystal was more difficult. This is mainly due to the steepness of the solidus curve at low N<sub>2</sub> percentages in the Ar-N<sub>2</sub> phase dia-

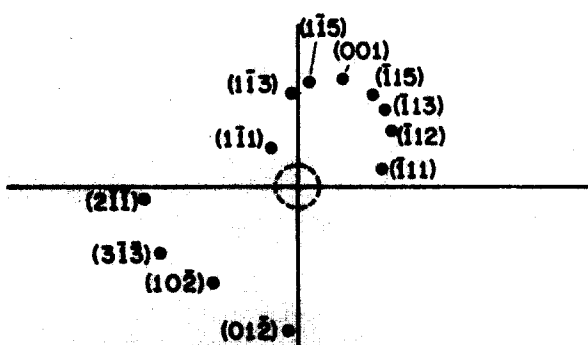
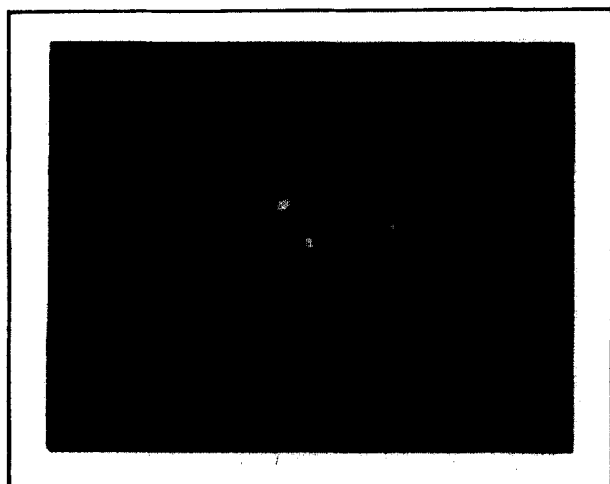


FIG. 2. Transmission Laue photograph of a fcc Ar-4% O<sub>2</sub> crystal. Below it are shown computer-fitted Laue spots labeled by Miller indices of the corresponding reflecting planes as determined by the orientation procedure.

gram. This required a large amount of N<sub>2</sub> in the initial Ar-N<sub>2</sub> gas mixture so that a reasonable amount of N<sub>2</sub> could be dissolved in the solid. Initial gaseous mixtures of Ar-10% N<sub>2</sub> and Ar-20% N<sub>2</sub> all resulted in the formation of fcc crystals. Finally, a gaseous mixture of Ar-30% N<sub>2</sub> was used to grow an Ar-5% N<sub>2</sub> crystal which was of the fcc phase. However, after growing the crystal to a height of about 7 mm, a subsequent slight decrease in the temperature resulted in the triggering of a transformation from the fcc to the hcp phase which started at the top. The transformation was clearly evident by observation of birefringence in the crystal. The boundary separating the two regions traveled downwards at about 2 mm/day. The transformation stopped when about 2 mm of nonbirefringent solid remained at the bottom while the rest of it had become birefringent. When the crystal was viewed under ordinary light there was no sign of a boundary or any other visual defects. Laue photographs taken in the bottom 2 mm region showed that this portion was still a good quality fcc crystal with the same initial orientation. On the other hand, Laue photographs taken near the top and middle of the crystal showed that the crystal transformed to the hcp phase was single but slightly strained. The angles between the (111) and (100) directions in the parent fcc crystal and the *c* axis of the hcp crystal were about 45° and 13°, respectively. This effect was also observed on another occasion for

Ar-5% N<sub>2</sub> (although no orientations were made the second time).

From the many attempts to grow single crystals of Ar alloys, some general comments can be made: (a) The cell used for crystal growth should be absolutely clean. The presence of even one or two tiny dust particles at the bottom favored polycrystalline samples. The installation of a dust trap (Fig. 1) improved the crystal growth success rate. (b) The cell should be vibration free. The presence of the slightest disturbance apparently perturbed equilibrium conditions and initiated freezing of a polycrystalline solid while increasing the incidence of stacking faults. (c) Contrary to the phase diagram of Barrett *et al.*,<sup>3,5</sup> the present results show that the fcc phase of Ar can accept at least about 4% O<sub>2</sub> and N<sub>2</sub> at the freezing point without any sign of the hcp phase. (d) Many crystals (which appeared to be single) could not be oriented either as fcc or hcp. This was especially true in the 4½%–5½% solid concentration range and was assumed to be due to stacking faults or fcc-hcp mixing. (e) For concentrations in the 5% range it was found that if the procedure of cooling from the gaseous phase to the formation of a seed was done in a continuous manner (i.e., without letting the liquid sit for a few hours near the freezing point), then reasonably good quality hcp crystals could be produced. Slower cooling tended to enhance stacking fault conditions in this range of con-

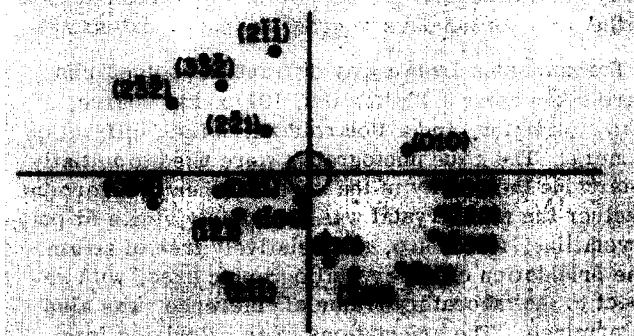
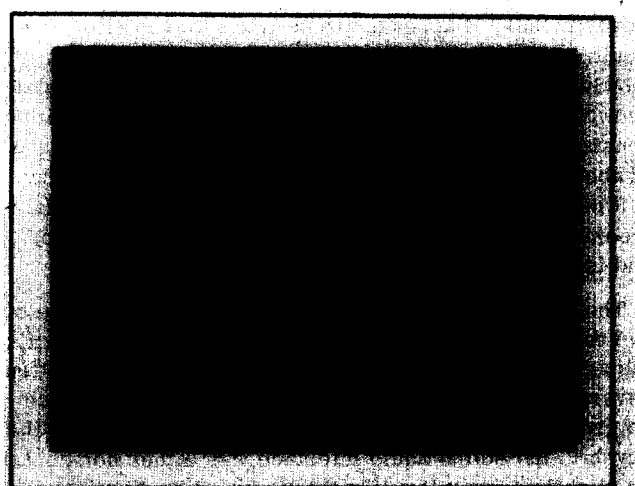


FIG. 3. Transmission Laue photograph of a hcp Ar-6% O<sub>2</sub> crystal. Below it are shown computer-fitted Laue spots labeled by Miller indices of the corresponding reflecting planes as determined by the orientation procedure.

centrations. (f) Single crystals of hcp Ar alloys could only be grown at about 6% (as low as 5% for continuous cooling) to 7% solid concentrations. Above about 7½%, dendritic growth problems usually resulted in polycrystalline samples.

## DISCUSSION

In the present work, it was not possible to obtain single crystals of hcp Ar alloys below about 5% concentration of O<sub>2</sub> in the solid and below about 4½% of N<sub>2</sub>. In all such cases, the crystals were found to be completely fcc. This is contrary to previous studies of Meyer *et al.*<sup>3-6</sup> Schuberth<sup>9</sup> also notes some discrepancy with Meyer's results. On Figs. 4 and 5, the vertical dotted line (fcc-hcp phase boundary) represents a suggested modification to the existing phase diagrams in the present context. This context being the growth of large single crystals from the melt, under quasiequilibrium conditions. These conditions are considerably different from those of Meyer and co-workers. In their work, the Ar mixtures were plastically deformed or homogenized by cold working and then annealed for several hours near the melting point, before using the x-ray diffraction powder technique for determining the structure. From the present work, especially from comment (e) above, it is evident that the hcp phase is more likely to result from continuous or slightly faster cooling, at least near the fcc-hcp boundary. Hence, the question of how equilibrium is approached in determining such a phase diagram is significant here.

In systems of this kind, where one phase is favored only marginally above another, it may indeed be the case that the phase diagram for large single crystals, grown under quasiequilibrium conditions, is not the same as that for cold-worked and annealed polycrystalline samples. Surface (or particle size) contributions could be significant.<sup>19</sup> Schuberth, in fact, states that from

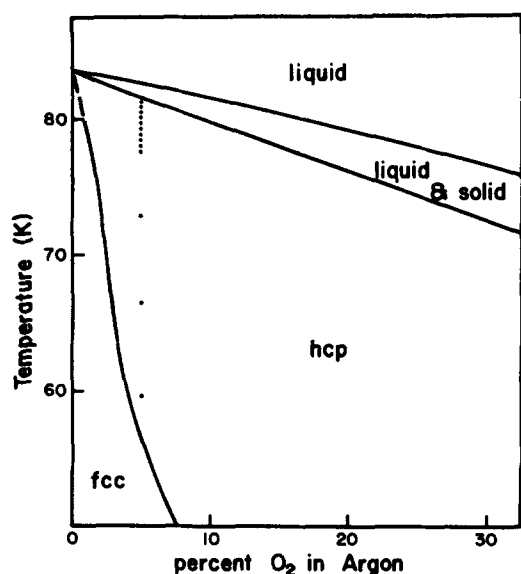


FIG. 4. Section of argon-oxygen phase diagram as obtained from Ref. 5. Vertical dotted line represents the fcc-hcp boundary in the context of the present work.

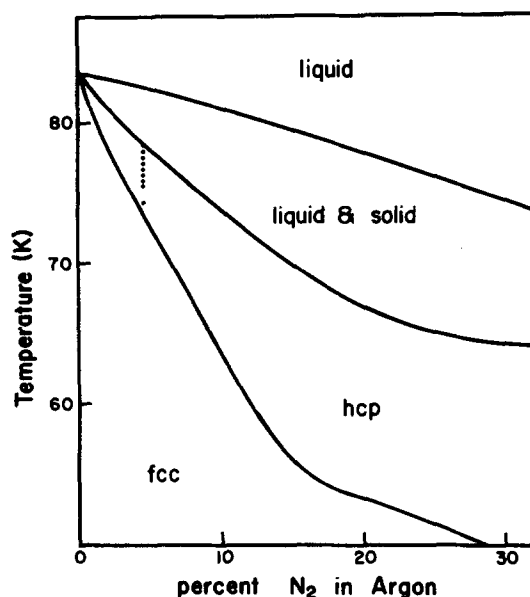


FIG. 5. Section of argon-nitrogen phase diagram as obtained from Ref. 3. Vertical dotted line represents the fcc-hcp boundary in the context of the present work.

the Ar-O<sub>2</sub> Raman intensity distribution, it appears that the hcp regions concentrate within less than 1 mm of the surface and are apparently predominantly surface induced.<sup>9</sup> As a further example, it is worth noting that, in their studies on the cobalt fcc-hcp transformation, Houska *et al.*<sup>20</sup> conclude that findings obtained on powder specimens do not necessarily apply to massive specimens.

Meyer<sup>6</sup> also comments that a peritectic reaction must occur in the range 0%-1% O<sub>2</sub> at a temperature around 82 ± 1 K, and that this area had not been investigated in detail because recrystallization and grain growth in this temperature range are too fast to allow the use of the powder method. In fact, from their phase diagram<sup>5</sup> it appears that the fcc-hcp boundary line was extrapolated from experimental points near 58 K and that no detailed studies at higher temperatures and concentrations up to 4% were done.

In the present work, it was also illustrated that a transformation from a single crystal fcc to a single crystal hcp can take place in a large sample. The orientations, on the one such case already described, yielded no evidence of massive shearing in the atomic array of the matrix or, in particular, the rearrangement (through slipping) of close-packed planes about the fcc (111) axis. According to Meyer,<sup>6</sup> phase transitions in Ar alloys are of the martensitic type and are very sensitive to strain which can enhance or retard it, as in the case of plastic deformation or fairly rapid cooling of the freezing liquid. These transformations, especially in van der Waal's lattices, are rarely complete. Hence, it was not surprising to find that the transformation left the lower portion of one of the crystals unchanged, while the hcp region was slightly strained. It must, however, again be emphasized that, initially, this particular crystal (at 5% N<sub>2</sub> concentration) formed a fcc structure from the melt under quasiequilibrium conditions. None of the

crystals were cooled to any significant degree due to the resulting development of strains (and consequent unreliability of the results).

Preliminary experiments on Ar-CO indicate behavior similar to that of Ar-N<sub>2</sub>.

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