Structure and compression of crystalline argon and neon at high pressure and room temperature

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Argon and neon crystallize in the face-centered cubic structure \( (Fm\overline{3}m, z = 4) \) at 11.5 \( \pm \) 0.5 and 47.4 \( \pm \) 0.5 kbar, respectively, at 293 K. Single-crystal cell dimensions were obtained at 82 kbar for argon and 144 kbar for neon with high-pressure, x-ray diffraction techniques. The data were corrected to 0 K and fitted to a second-order Murnaghan equation of state with \( V_0 \) and \( K_0 \) constrained to results obtained in low-temperature experiments. No solid-solid phase transitions are observed to the highest pressures studied.

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Rare-gas solids (RGS) have been studied extensively, especially with regard to their \( P-T-V \) equations of state (EOS).

Most of these investigations, however, have been performed under cryogenic conditions. A diamond-window, high-pressure cell (diamond cell) has been modified for the x-ray study of compounds that are normally gaseous under ambient conditions.

Data are given, therefore, on the variation of argon and neon cell constants as a function of pressure of 293 K. These data are also used to calculate a 0-K equation of state.

Single crystals of RGS were produced in a cryogenic, diamond-anvil cell, wherein liquefied Ne or Ar was contained in T301 stainless-steel gaskets (with apertures 0.25 mm thick and 0.30 mm in diameter).

Argon and neon were liquefied in a helium atmosphere. No contamination of the Ne and Ar samples by helium was observed, on the basis of previously reported freezing pressures of pure gases at 293 K.

At 293 K a single crystal of argon formed from liquid at 11.5 \( \pm \) 0.5 kbar in the gasketed sample chamber. In similar experiments on neon a single crystal formed from liquid at 47.4 \( \pm \) 0.5 kbar. Both Ar and Ne crystals were clear and colorless, displayed no grain boundaries, and had no birefringence. X-ray diffraction maxima for argon were sharp at all pressures to 80 kbar, though some spot diffuseness was observed above 80 kbar. Sharp diffraction maxima were observed for neon to 144 kbar.

Rare-gas solids were studied by x-ray diffraction photography and four-circle diffractometry. Crystals were oriented with precession photographs, and cubic unit-cell dimensions were determined either from reflection centering on the automated diffractometer or from measurements on film. Unit-cell volumes determined from film measurements are usually accurate to within 0.05\%, whereas those from diffractometry may be better than 0.02\%. Diffractometry takes several hours, compared with the few minutes required for the film measuring procedure; at higher pressures some occurrences of slow leakage of the pressurized gases favor the latter procedure.

Pressure was measured to within \( \pm \) 0.5 kbar from the calibrated wavelength shift of the \( R_\lambda \) fluorescence lines of small ruby crystals included in the mount.

Room temperature was 293 \( \pm \) 1 K over the period of study.

The positions and intensities of x-ray diffraction maxima are consistent with both Ar and Ne having the face-centered cubic metal structure. Values of unit-cell dimensions

<table>
<thead>
<tr>
<th>Pressure (kbar)</th>
<th>( a ) (Å)</th>
<th>( V ) (cm(^3)/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.5(5)</td>
<td>Crystals and liquid coexist</td>
<td></td>
</tr>
<tr>
<td>12.8(6)</td>
<td>5.086(5)</td>
<td>19.819(16)</td>
</tr>
<tr>
<td>14.2(3)</td>
<td>5.072(4)</td>
<td>19.651(4)</td>
</tr>
<tr>
<td>17.1(5)</td>
<td>4.987(4)</td>
<td>18.680(4)</td>
</tr>
<tr>
<td>21.1(1)</td>
<td>4.933(10)</td>
<td>18.075(7)</td>
</tr>
<tr>
<td>24.2(2)</td>
<td>4.903(4)</td>
<td>17.752(1)</td>
</tr>
<tr>
<td>29.0(5)</td>
<td>4.835(4)</td>
<td>17.029(1)</td>
</tr>
<tr>
<td>33.3(2)</td>
<td>4.795(10)</td>
<td>16.600(7)</td>
</tr>
<tr>
<td>33.8(2)</td>
<td>4.791(2)</td>
<td>16.568(2)</td>
</tr>
<tr>
<td>36.1(3)</td>
<td>4.778(5)</td>
<td>16.430(3)</td>
</tr>
<tr>
<td>38.0(2)</td>
<td>4.755(15)</td>
<td>16.188(10)</td>
</tr>
<tr>
<td>38.5(2)</td>
<td>4.751(10)</td>
<td>16.153(7)</td>
</tr>
<tr>
<td>44.1(2)</td>
<td>4.714(8)</td>
<td>15.777(5)</td>
</tr>
<tr>
<td>47.7(1)</td>
<td>4.683(20)</td>
<td>15.468(13)</td>
</tr>
<tr>
<td>50.0(3)</td>
<td>4.667(8)</td>
<td>15.31(5)</td>
</tr>
<tr>
<td>55.5(5)</td>
<td>4.643(20)</td>
<td>15.071(13)</td>
</tr>
<tr>
<td>63.4(3)</td>
<td>4.603(8)</td>
<td>14.69(5)</td>
</tr>
<tr>
<td>67.8(4)</td>
<td>4.593(20)</td>
<td>14.590(13)</td>
</tr>
<tr>
<td>71.2(1)</td>
<td>4.583(20)</td>
<td>14.494(13)</td>
</tr>
<tr>
<td>81.7(6)</td>
<td>4.544(4)</td>
<td>14.128(25)</td>
</tr>
</tbody>
</table>

Ar

Crystals and liquid coexist

Neon

Crystals and liquid coexist

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TABLE I. Unit-cell edge and molar volume for crystalline argon and neon at 293 K.

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measured at 19 pressures for Ar and 14 pressures for Ne are recorded in Table I.

A remarkable property of Ar and Ne is that with any change of pressure greater than 3 or 4 kbar (i.e., a volume change of 1 or 2%) the sample recrystallized to a new single crystal or a small group of crystals with one large individual. Rather than support the stress generated by a deforming gasket with changing pressure, the sample recrystallized and thus conformed with the changing shape of the sample chamber. Furthermore, the crystal usually formed within ± 2° of one of the two orientations with respect to the flat diamond-anvil faces. In half of the runs a (220) plane was parallel to the randomly oriented, polished diamond anvils. Next in frequency of orientation was the (111) plane, which is the plane of closest packing. A third plane, oriented parallel to diamonds in four (13%) of the runs, is (211). The (100) plane, on the other hand, was never within 15° of the anvil surfaces. These nonrandom crystallization directions probably occurred as a result of the uniaxial stress associated with the diamond-anvil design and do not appear to be the result of epitaxial growth on the diamonds.

Data from Table I may be used to calculate equation-of-state parameters of crystalline Ar and Ne in terms of the bulk modulus at the freezing pressure and its pressure derivatives. A more useful approach, however, is to correct the observed pressure for effects of temperature and zero-point vibration energy using the equation of state

$$P(V, T) = P_s(V) + P_v(V) = P_t(V, T),$$

where $P_s$ is the static pressure, $P_v$ is the zero-point vibration pressure, and $P_t$ is the so-called thermal pressure. In the Debye approximation,

$$P_s(V) = (9\gamma /8V)R\Theta(V),$$

$$P_v(V) = (3RT\gamma /V)D(\Theta /T),$$

and

$$D(\Theta /T) = \left(\frac{T}{\Theta}\right)^3 \int_0^\Theta \frac{x^4 dx}{e^x - 1},$$

where $r$ is the gas constant, $\Theta$ is the Debye temperature, $D$ is the Debye function, $\gamma$ is the Grüneisen parameter, and $T$ is the absolute temperature. If $\gamma$ is given by $\gamma = (V/V_0)\gamma_1 + \frac{1}{3}$,

as suggested by Holt and Ross$^6$ and Kopyshov,$^7$ with $\gamma_1$ independent of volume, then the Debye temperature is given by

$$\Theta(V) = \Theta_0 \left(\frac{V_0}{V}\right)^{1/3} e^{\gamma_1 \left(1 - \frac{V}{V_0}\right)},$$

where $\Theta_0$ is the Debye temperature at $V_0$. Equations (1)–(5) have been used to calculate $P_s$ for each of the observed volumes. These data were then fitted to a second-order Murnaghan equation of state of the form

$$P_s - P_{s0} = 2K_0 \left[\left(\frac{V_0}{V}\right)^q - 1\right] - K'' \left[\left(\frac{V_0}{V}\right)^q - 1\right]^{-1},$$

where $K_0$, $K''$, and $K_0''$ are the zero Kelvin static bulk modulus and its pressure derivatives. For neon and argon, $V_0$ and $K_0$ were fixed at the low-temperature results derived from the x-ray diffraction studies of Batchelder et al.$^9$ and Peterson et al.$^{10}$ respectively. The Table II lists the values of the parameters, and Figs. 1 and 2 are isothermal plots of the results. The present data gree with the results of Anderson and Swenson.$^8$

RARE-gas solids may prove to be excellent hydrostatic pressure media in future diamond-anvil cell experiments. The RGS are extremely compressible and produce a hydro-

![FIG. 1. Calculated isotherms for neon (squares are 293 K observed values).](image1)

![FIG. 2. Calculated isotherms for argon (squares are 293 K observed values).](image2)

### Table II. Equation-of-state parameters for crystalline neon and argon.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Neon</th>
<th>Argon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_0$ (cm$^3$/mole)</td>
<td>13.394$^a$</td>
<td>22.557$^a$</td>
</tr>
<tr>
<td>$\Theta_0$ (K)</td>
<td>75.1$^a$</td>
<td>93.3$^a$</td>
</tr>
<tr>
<td>$\gamma_1$</td>
<td>2.05$^a$</td>
<td>2.20$^a$</td>
</tr>
<tr>
<td>$P_{s0}$ (kbar)</td>
<td>-1.137</td>
<td>-1.0289</td>
</tr>
<tr>
<td>$K_0$ (kbar)</td>
<td>7.437$^a$</td>
<td>23.701$^a$</td>
</tr>
<tr>
<td>$K''_0$ (kbar$^{-1}$)</td>
<td>7.071 ± 0.057</td>
<td>6.97 ± 0.11</td>
</tr>
<tr>
<td>$K''_2$ (kbar$^{-1}$)</td>
<td>-0.051 ± 0.004</td>
<td>-0.040 ± 0.010</td>
</tr>
</tbody>
</table>


static environment at high pressure, on the basis of the
sharpness of x-ray diffraction maxima. Furthermore, lattice
constants of these cubic phases are very sensitive to pressure
and may be used as an internal pressure calibration. In addi-
tion, it may be possible to derive a fundamental equation of
state for these materials from first principles. In that case,
the lattice constants of these phases would constitute a pri-
mary pressure standard.

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