

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 ($Fm\bar{3}m$, $z = 4$) at 11.5 ± 0.5 and 47.4 ± 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).¹ 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.^{2,3} 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).³ 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.¹

At 293 K a single crystal of argon formed from liquid at 11.5 ± 0.5 kbar in the gasketed sample chamber. In similar experiments on neon a single crystal formed from liquid at 47.4 ± 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 diffractometer⁴ 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 ± 0.5 kbar from the

calibrated wavelength shift of the R_1 fluorescence lines of small ruby crystals included in the mount.⁵ Room temperature was 293 ± 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 I. Unit-cell edge and molar volume for crystalline argon and neon at 293 K.

Pressure (kbar)	a (Å)	V (cm ³ /mole)
Argon		
11.5(5)	Crystals and liquid coexist	
12.8(6)	5.0868(20)	19.819(16)
14.2(3)	5.0724(5)	19.651(4)
17.1(5)	4.9874(5)	18.680(4)
21.1(1)	4.9330(10)	18.075(7)
24.2(2)	4.90344(5)	17.752(1)
29.0(5)	4.83594(5)	17.029(1)
33.3(2)	4.7950(10)	16.600(7)
33.8(2)	4.7919(2)	16.568(2)
36.1(3)	4.7785(5)	16.430(3)
38.0(2)	4.7550(15)	16.188(10)
38.1(2)	4.7516(10)	16.153(7)
44.1(2)	4.714(8)	15.77(5)
47.7(1)	4.6834(20)	15.468(13)
50.0(3)	4.667(8)	15.31(5)
55.9(5)	4.6430(20)	15.071(13)
63.4(3)	4.603(8)	14.69(5)
67.8(4)	4.5930(20)	14.590(13)
71.2(1)	4.5830(20)	14.494(13)
81.7(6)	4.544(4)	14.128(25)
Neon		
47.5(4)	Crystals and liquid coexist	
48.3(5)	3.7860(20)	8.171(9)
58.4(4)	3.727(1)	7.795(4)
62.2(4)	3.7007(5)	7.631(2)
68.1(3)	3.684(3)	7.529(12)
72.0(3)	3.6614(10)	7.391(4)
72.3(5)	3.6499(10)	7.321(4)
77.1(4)	3.6424(20)	7.276(8)
80.1(3)	3.6361(10)	7.239(4)
87.7(4)	3.6101(20)	7.085(8)
87.9(5)	3.6007(30)	7.029(12)
110.0(5)	3.543(2)	6.697(8)
121.6(5)	3.516(2)	6.545(7)
133.1(5)	3.494(2)	6.423(7)
144.2(5)	3.472(2)	6.302(7)

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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 $\pm 2^\circ$ 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 anvil. 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

$$P(V, T) = P_s(V) + P_z(V) = P_T(V, T), \quad (1)$$

where P_s is the static pressure, P_z is the zero-point vibration pressure, and P_T is the so-called thermal pressure. In the Debye approximation,

$$P_z(V) = (9\gamma/8V)R\Theta(V), \quad (2)$$

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

and

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

where r is the gas constant, Θ is the Debye temperature, D is the Debye function, γ is the Grüneisen parameter, and T is the absolute temperature. If γ is given by $\gamma = (V/V_0)\gamma_1 + \frac{1}{2}$,

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

Parameter	Neon	Argon
V_0 (cm ³ /mole)	13.394 ^a	22.557 ^b
Θ_0 (K)	75.1 ^c	93.3 ^d
γ_1	2.05 ^c	2.20 ^c
P_{z0} (kbar)	-1.337	-1.0289
K_0 (kbar)	7.437 ^a	23.701 ^b
K'_0	7.071 \pm 0.057	6.97 \pm 0.11
K''_0 (kbar ⁻¹)	-0.051 \pm 0.004	-0.040 \pm 0.010

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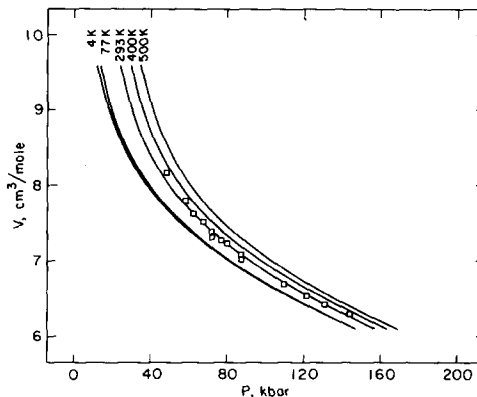


FIG. 1. Calculated isotherms for neon (squares are 293 K observed values).

as suggested by Holt and Ross⁶ and Kopyshv,⁷ with γ_1 independent of volume, then the Debye temperature is given by

$$\Theta(V) = \Theta_0 \left(\frac{V_0}{V}\right)^{1/2} e^{\gamma_1 \left(1 - \frac{V}{V_0}\right)} \quad (5)$$

where Θ_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 Muraghan equation of state of the form

$$P_s - P_{z0} = 2K_0 \left[\left(\frac{V_0}{V}\right)^q - 1\right] \left\{ q \left[\left(\frac{V_0}{V}\right)^q + 1\right] - K'_0 \left[\left(\frac{V_0}{V}\right)^q - 1\right] \right\}^{-1}, \quad (6)$$

$$q = (K_0'^2 - 2K_0 K_0'')^{1/2},$$

where K_0 , $K'_0 \leq$ 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 agree 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-

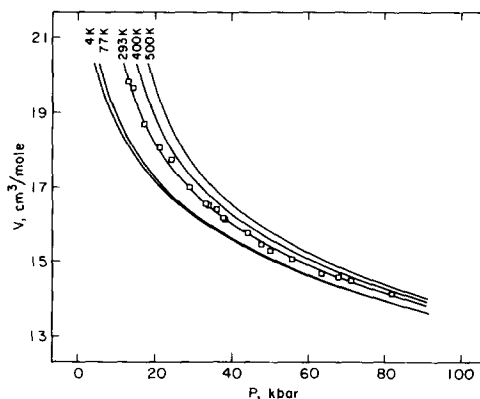


FIG. 2. Calculated isotherms for argon (squares are 293 K observed values).

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 addition, 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 primary pressure standard.

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