High Pressure Measurements of the He-Ne Binary Phase Diagram at 296 K: Evidence for the Stability of a Stoichiometric Ne(He)$_2$ Solid

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The binary phase diagram of He-Ne mixtures has been measured at 296 K in a diamond anvil cell. It is of the eutectic type with no fluid-fluid separation of phases. A homogeneous solid mixture is shown to be stable for a mole fraction of He equal to $\frac{2}{3}$. Single-crystal synchrotron x-ray measurements indicate that this solid is ordered with 12 atoms in the unit cell. Gibbs free energy calculations support the attribution to the MgZn$_2$ type structure. It is the first Laves phase observed in a van der Waals molecular compound.

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The study of mixtures at high density is related to a rich class of condensed matter phenomena and it is also directly relevant to modeling the interior of the giant planets. Moreover, this field presents important practical interest for mastering detonic and alloy synthesis processes. But quantitative theoretical calculations for mixed systems are still less satisfactory than those involving a single species. So, experimental information on the properties of binary mixtures of simple systems, such as He-Ne, under high pressure is particularly desirable in order to test and refine their theoretical description. Until recently, such measurements were usually limited to the fluid phase below 1 GPa [1]. But thanks to the development of the diamond anvil cell (DAC), it was recently possible to extend these investigations to much higher pressures. Measurements of H_2-He [2,3], He-N_2 [4], N_2-O_2 [5], and H_2-Ne [6] binary mixtures in a DAC have already been reported. We present here the optical determination of supercritical separation of phases in He-Ne mixtures, namely, its binary phase diagram at 296 K. These results establish the unexpected stability of a homogeneous solid at a molar concentration of He equal to $\frac{2}{3}$. Using single-crystal synchrotron x-ray diffraction, this Ne(He)$_2$ solid is shown to be ordered with a tetramolecular hexagonal unit cell. Its structure can be almost certainly attributed to the MgZn$_2$ type Laves phase; Gibbs free energy calculations support this attribution.

The membrane diamond anvil cell has been used for generating the static high pressures. Its design and loading system have been presented elsewhere [7]. As was demonstrated in our work on H_2-He mixtures [2], this device is particularly well adapted for studying separation of phases at a given temperature, whereas with other DAC such measurements require one to work at variable temperatures. The initial mixture was prepared in a gas container under a pressure of 16 MPa and stabilized for at least 36 h. The concentration was calculated from the partial pressure of the two gases, taking into account the deviation from ideal mixing with the second virial coefficients (this could amount to a correction of 2 mol%). Stainless-steel T301 gaskets were used and the pressure was measured by the quasihydrostatic ruby scale [8]. The phase transitions were detected by visual observation through a microscope setup: The illumination with the 488-nm Ar^+ laser line gives a good contrast for the projection of the sample chamber on the screen. Solid-fluid equilibrium, $S+F$, could be easily seen. The pressure of the $F+S$ separation of phases was taken as that measured when a small solid was in equilibrium with the fluid, at the limit of its disappearance. The solid-solid separation of phases, $S+S$, which occurs at a higher pressure than the $S+F$ separation of phases, was investigated by slowly raising the pressure from a $S+F$ equilibrium just above the $S+F$ boundary line. Still, the location of the $S+F \rightarrow S+S$ transition was harder to measure precisely.

Our measurements of the He-Ne binary phase diagram at 296 K are shown in Fig. 1. Through a first examination, the phase diagram is seen to be of the eutectic type with a total miscibility of He and Ne in the fluid phase. These results complete previous experiments on the supercritical properties of the series He–rare-gas fluid mixtures, He-Ar [9], He-Kr [10], and He-Xe [11]. The fluid-fluid separation of phases is seen to increase from zero for He-Ne mixtures to practically total for He-Xe mixtures. This can be simply understood in terms of a geometrical analysis which directly relates the miscibility of the two components to the difference of their pair interactions [6]. A great advantage of the DAC technique is that the mutual solubility in the solid phase can also be investigated. The maximum solubility of He in solid Ne, S_1, is observed to increase from 6 ± 1 mol% at 5 GPa to around 12 ± 2 mol% at 16 GPa. The solubility of Ne in solid He, S_2, is smaller and slightly increasing from 3 ± 1 mol% at 12 GPa to 4 ± 1 mol% at 16 GPa. The accura-

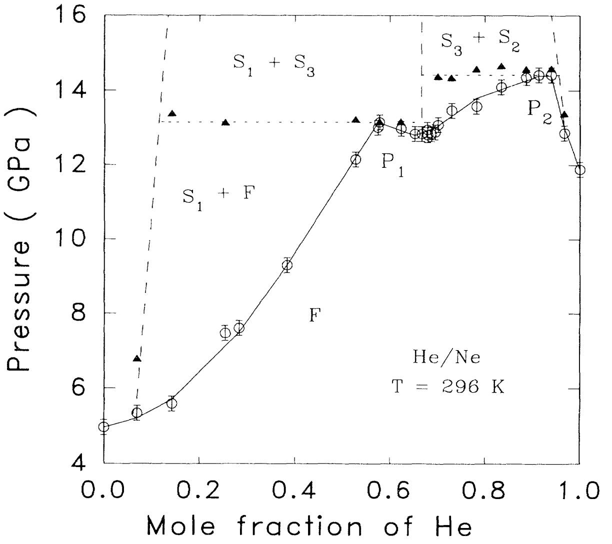

FIG. 1. He-Ne binary phase diagram at 296 K. The circles correspond to our measurements of the $F \rightarrow S+F$ transition; the solid line which interpolates between them indicates the $S+F$ boundary line. The triangles are data points on the solid boundary lines: The left and right large dashed lines limit the stability domains, respectively, of a rich Ne solid, S_1, and of a rich He solid, S_2, and the one in between indicates the location of the stable $Ne(He)_2$ solid, S_3; the small dashed lines are the boundary lines above which a solid-solid separation of phases is observed.

cy of such a determination is, however, limited by the inherent metastability known to take place in solid-solid separation of phases.

For all the concentrations studied, the homogeneous fluid mixture separates first into an $S+F$ equilibrium over a certain pressure interval except for the He concentration of 66.6 mol% where an $F \rightarrow S$ transition is observed. The $S+F$ boundary line is drawn as a solid line in Fig. 1. Surprisingly, it is of convex shape between the two eutectic points P_1 (≈ 58 mol%, 13.2 GPa) and P_2 (≈ 93 mol%, 14.5 GPa) with a minimum around 66.6 mol%; that is incompatible with the sole S_1+F or S_2+F separation of phases. This seems to imply that a homogeneous solid mixture should be stable for a He concentration in between P_1 and P_2. Further experimental investigations were performed in order to prove this. For a mole fraction of He equal to $\frac{2}{3}$, the fluid mixture is observed to crystallize into a homogeneous solid which then melts at a fixed pressure, 12.8 GPa. Departing positively or negatively from this He molar concentration of $\frac{2}{3}$, the pressure interval, over which the $S+F$ equilibrium exists, increases and rises further in pressure, a more contrasted solid-solid separation of phase is observed whereas this $Ne(He)_2$ solid remains homogeneous up to the maximum pressure investigated, 25 GPa. Consequently, we can assert that for a He molar concentration of $\frac{2}{3}$, a homogeneous solid is stable, noted as S_3 in Fig. 1. It is of interest to establish whether this solid phase corresponds to a regular arrangement of atoms or to a disordered solid solution.

TABLE I. Observed and calculated lattice spacings at 13.7 GPa of the $Ne(He)_2$ compound. The unit cell is hexagonal with $a = 4.066(5)$ Å and $c = 6.616(5)$ Å.

hkl	d_{obs}	d_{cal}
101	3.1072	3.107
102	2.4113	2.411
103	1.8694	1.870
112	1.7322	1.731
203	1.3762	1.376
212	1.2346	1.234
213	1.1396	1.139
215	0.9382	0.938

The method of achieving x-ray diffraction of low Z elements under high pressure in a DAC involves a combination of single-crystal and energy dispersive diffraction techniques with the high brilliance of the polychromatic x-ray radiation generated from a synchrotron source [12]. A crystal of the ($\frac{2}{3}$ He, $\frac{1}{3}$ Ne) mixture was grown by raising the pressure at room temperature in the MDACX [13]. Strong reflections, including multiple higher-order peaks, were obtained from the solid at 13.7 and 21.8 GPa with the high flux of the wiggler x-ray beamline X17C of the National Synchrotron Light Source. The reflections had sharp rocking curves of about 0.05°, indicative of good quality crystals (the sample consisted of at least two large single crystals). This proves that the $Ne(He)_2$ solid is an ordered phase. Furthermore, as seen in Table I, the observed d spacings are attributed to the (101), (102), (103), (112), (203), (212), (213), and (215) classes of a hexagonal unit cell, with an almost ideal c/a ratio. The unit cell has the following dimensions: $a = 4.066$ Å, $c = 6.616$ Å at 13.7 GPa and $a = 3.885$ Å, $c = 6.328$ Å at 21.8 GPa. The volume per atom of the $Ne(He)_2$ solid should not differ much from the ideal mixing value, estimated to be equal to 4.80 cm^3/mole at 13.7 GPa from the equation of state of He [14] and Ne [15]. Using this value, the number of atoms in the unit cell is found to be 11.9, the deficiency from the integral number being due to the excess volume of mixing. Consequently, the structure of the $Ne(He)_2$ solid has 12 atoms in the unit cell. The detailed arrangement of the atoms in the unit cell could be obtained from the measurement of the intensity relation of the reflections. But this remains difficult with the present technique. The structure assignment is done below from thermodynamic considerations.

Clearly, there exist a great variety of RX_2 structures, but if the principle of maximization of packing fraction alone is applied [16], a much smaller number of structures is expected to form. These are either of substitutional or interstitial type depending on the ratio of the atomic diameters of the two components. If the atomic diameters d_A and d_B are approximately in the ratio 1.2:1, a class of substitutional AB_2 compounds should be expected, usually referred to as Laves phases [17]. The Laves phases crystallize in one of three closely related structures, isomorphous with the compounds $MgCu_2$ (cubic with 24 atoms in the unit cell), $MgZn_2$ (hexagonal with 12 atoms in the unit cell), or $MgZn_2$ (hexagonal with 24 atoms in the unit cell). On the other hand, if d_B/d_A is in the interval [0.48,0.62] an interstitial phase should be stable, isomorphous with the AlB_2 structure [18] (hexagonal with 3 atoms in the unit cell). In the solid phase at high pressure, the effective atomic diameter is given by the nearest-neighbor distance; this gives for Ne-He, around 15 GPa, a ratio $d_{Ne}/d_{He}=1.19$ which fits the Laves condition. The hexagonal structure of $Ne(He)_2$ with 12 atoms in the unit cell is thus almost certainly the $MgZn_2$ type. Below, more quantitative Gibbs free energy calculations support this assignment.

The exact determination of the Gibbs free energy of a solid mixture is certainly a computationally demanding task since the Gibbs free energy differences involved in phase separation are quite small. We have chosen instead to use an anisotropic cell model with quantum corrections, recently named the local harmonic model [19]. It offers accurate free energies and equations of state (outside the near melting region) with computational efficiency. Furthermore, the errors inherent in the model could somehow cancel out in the comparison of the free energies of the various phases. Three ordered AB_2 structures are considered: two Laves phases, the cubic $MgCu_2$ type structure and the hexagonal $MgZn_2$ type structure, and the interstitial AlB_2 type structure. The solid phase diagram is then obtained by comparing the Gibbs free energies of these three ordered structures and of the solid solutions. For a solid solution, the simplest model is based upon the assumption of substitutional alloy with a random distribution on sites, named the regular mixture. But in fact, real mixtures are not truly random or purely substitutional and so the regular mixture model ignores local correlations in the distribution of the constituent atoms. In the fluid phase, however, it was shown that the Gibbs free energy of a mixture can be accurately calculated without having to determine these local correlations if an effective pure fluid (EPF or van der Waals 1 fluid) theory is used: For exp-6 [exponential-$1/r^6$) interactions, the mixing rules for the parameters of the effective potential are $\langle r^3\rangle$, $\langle \varepsilon r^3\rangle$, and $\langle \varepsilon r^3 \alpha\rangle$ [20]. Knowing that at high density the local environment of an atom in the fluid phase and in the solid phase are very similar, we have straightforwardly extended this effective one-component mixture to the solid phase, under the name effective pure solid (EPS) model. This EPS model was recently used to calculate the miscibility of H_2 and He in their solid phases [21], giving good agreement with experiment.

For high-pressure applications, the exp-6 potential has been successfully used for the adjustment of effective pair interactions on experiment. Such potentials have been proposed for He [22] ($\alpha=13.1$, $\varepsilon=10.8$ K, $r_m=2.9673$ Å) and for Ne [23] ($\alpha=13.2$, $\varepsilon=42.0$ K, $r_m=3.18$ Å). For the He-Ne exp-6 potential, two different parameter sets were used: The first one is given by the Lorentz-Berthelot mixing rule ($\alpha=13.15$, $\varepsilon=21.297$ K, $r_m=3.073$ Å) and the second one is fitted on the recently proposed He-Ne pair potential of Kiel [24] of the so-called HFD-B form ($\alpha=13.70$, $\varepsilon=21.179$ K, $r_m=3.023$ Å). The results of the calculations are almost essentially the same for the two He-Ne parameter sets over the pressure range investigated here, 10–25 GPa. This is seen in Fig. 2 where the x-ray equation of state (EOS) is compared with the ones calculated for the $MgZn_2$ type structure with the two Ne-He potentials (the solid line corresponding to the Berthelot-Lorentz potential and the dashed line to the Kiel one). The experimental EOS is lower than the calculated ones: This reflects the fact that the repulsive wall of the Ne-He should be softer, as expected if many-body interactions were effectively taken into account in the potential. Still, more x-ray data or Brillouin scattering measurements of the sound velocity of He-Ne mixtures (also in progress in our laboratory) are necessary for a meaningful adjustment of a real exp-6 He-Ne interaction. In Fig. 3, excess Gibbs free energies of mixing, $\Delta G^E(x)$, at 15 GPa is reported for the various models [the EPS mixture for the solid solutions and the $MgZn_2$, $MgCu_2$, and AlB_2 type structures for the stoichiometric $Ne(He)_2$ solid with the Berthelot-Lorentz Ne-He potential]. The phase boundary of mutual solubility in the solid phase is given by the pair of compositions at which the tangent to $\Delta G^E(x)$ (as dashed lines) is passing

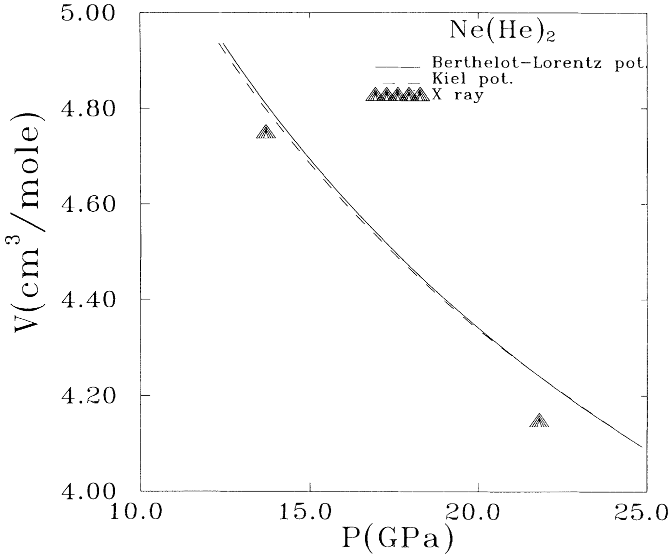

FIG. 2. Equation of state of $Ne(He)_2$ compound. The multiple-triangle symbols indicate the x-ray measurements. The solid line and dashed line represent calculations for the $MgZn_2$ type structure with the two He-Ne exp-6 potential parameters considered, respectively, the Berthelot-Lorentz one and the one adjusted on the Kiel pair potential [24].

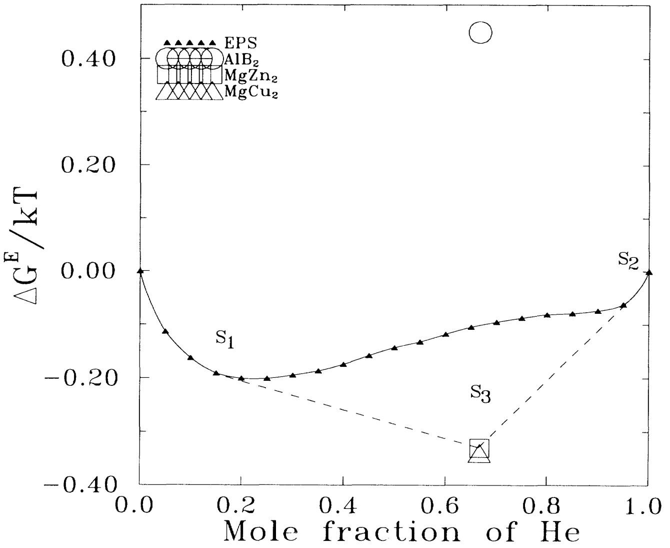

FIG. 3. Excess Gibbs free energy calculations, with the Lorentz-Berthelot He-Ne potential, for He-Ne mixtures in the solid phase at 15 GPa. The solid-triangle line corresponds to the EPS cell model of solid solutions. The square, triangle, and circle are the cell model calculations for the $Ne(He)_2$ stoichiometric compound, S_3, in the $MgZn_2$ hexagonal, $MgCu_2$ cubic, and AlB_2 hexagonal type structures, respectively. The dashed lines indicate the Maxwell construction for the phase boundary of homogeneous solid solutions, S_1 and S_2.

through the excess Gibbs free energy of the stable $Ne(He)_2$ structure. This Maxwell construction gives stable solid solutions, S_1 for He concentrations lower than 16 mol% and S_2 for He concentrations greater than 96 mol%, in very good agreement with experiment (respectively, 12 and 96 mol%). The two closely related $MgZn_2$ and $MgCu_2$ structures are both stable relative to the phase separation in S_1+S_2, with almost the same value of ΔG^E. The AlB_2 type structure, on the other hand, is seen to be unstable. The conclusion of these quantitative calculations is in agreement with the simple size ratio considerations: This is going to be helpful for a preliminary search of other Laves phases in van der Waals molecular compounds. During the course of this study, Vos *et al.* [25] have reported the discovery of a substitutional stoichiometric van der Waals molecular compound, $He(N_2)_{11}$. Both these new classes of molecular alloys, substitutional and interstitial, are of potential interest for improving the description of dense mixtures and could have unexpected applications for planetary physics.

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