# Desorption Behavior of Quench-Condensed Argon-Neon Mixtures

J. Meier, G. Wittich, J. Classen, and S. Hunklinger
*Kirchhoff-Institut für Physik, Universität Heidelberg, Albert-Ueberle-Strasse 3-5, 69120 Heidelberg, Germany*

(Received 30 July 2001; published 20 December 2001)

The desorption behavior of quench-condensed rare gas films has been investigated using high frequency surface acoustic waves. Measurements of pure films of argon and neon and of the binary mixture $\mathrm{Ar}_{1-c}/\mathrm{Ne}_c$ have been carried out. For small and very large neon concentration $c_{\mathrm{Ne}}$ a behavior is found which indicates the existence of a substitutionally disordered solid. In contrast, in the wide range of concentration $0.25 < c_{\mathrm{Ne}} < 0.92$ two discrete temperatures for neon desorption exist. The data clearly indicate the occurrence of two separate phases, one of pure neon, the other of crystallites with either $\mathrm{Ar}_2\mathrm{Ne}$ or $\mathrm{Ar}_3\mathrm{Ne}$ structure.

DOI: 10.1103/PhysRevLett.88.016104 PACS numbers: 68.03.Fg, 61.43.–j, 64.75.+g

Rare gas crystals are often used as model systems for condensed matter because of their simple interatomic interaction. This holds also for binary rare gas mixtures. To predict the equilibrium configuration of such systems several groups have developed molecularly based theories and simulation techniques using the hard sphere model [1–3] or the Lennard-Jones potential [4,5]. The main goal of these papers was to study the influence of the ratio $\alpha$ of the atomic radii of the two components as well as the impact of their binding energies on the structure [6,7] or the phase equilibrium [8]. For size ratios $\alpha > 0.85$ the predicted structure is a substitutionally disordered solid; i.e., both components form a crystal with a single phase where the atoms may substitute for one another arbitrarily on the lattice [2,9]. For smaller size ratios phase separation occurs. For certain values of $\alpha$ substitutionally ordered solids of the form $AB$, $AB_2$, and $AB_{13}$ are predicted to be stable, in some cases in combination with a pure phase of one component [1,10–12]. The $AB_2$ and $AB_{13}$ superlattice formations have been found experimentally for binary mixtures of hard sphere colloids [13].

Quench-condensed rare gas films are systems far away from thermodynamical equilibrium. Pure Ne or Ar films grow in a polycrystalline fcc configuration [14]. Computer simulations predict a high degree of porosity [15,16] and, on annealing, an increase of density due to structural relaxation [17]. These predictions have been confirmed by various experiments [18,19]. X-ray scattering experiments on quench-condensed argon/xenon mixtures demonstrate the occurrence of an amorphous phase over a wide range of concentration $30\% < c_{\mathrm{Ar}} < 80\%$ [20] which is frozen in due to the large difference between the atomic radii of the two elements ($\alpha = 0.88$) [21]. Since the system Ar/Ne has an even smaller size ratio $\alpha = 0.82$ it may be assumed that such mixtures condensate in an amorphous configuration over a wide range of concentration, too.

To our knowledge there exists only one publication reporting on the desorption behavior of a quench-condensed binary rare gas mixture [22]: In an ellipsometric measurement on a $\mathrm{Xe}_{90}\mathrm{Ar}_{10}$ mixture the two components were found to desorb separately at the respective desorption temperatures of the pure components. In this Letter we report on the desorption of quench-condensed Ar/Ne mixtures which show in a wide range of concentration a remarkably different behavior.

A $\mathrm{LiNbO}_3$ surface acoustic wave (SAW) device with gold interdigital transducers was mounted on the mixing chamber of a dilution cryostat. A pulse-echo technique with phase sensitive detection and a digital phase locked loop was used to measure the relative change of Rayleigh wave velocity $\delta v/v$ at a frequency $f = 109$ MHz. Locking of the phase was achieved by tuning the excitation frequency; in this way the change of sound velocity $\delta v/v$ is equal to the relative frequency shift $\delta f/f$.

For the condensation of films a capillary was led through the vacuum pumping tube which ended about 5 cm in front of the SAW device in a cylindrical cup covered with a fine mesh. Film growth was monitored by the decrease of sound velocity due to the mass load of the condensing rare gas atoms [23] and controlled with an accuracy better than 0.1 monolayer. Typical growth rates were of the order of 1 nm/min, typical film thicknesses $h \approx 100$–$200$ nm; the resulting relative change of frequency was of the order $\delta f/f \approx 10^{-3}$ at 109 MHz. During condensation the substrate temperature was held at 1 K. The gas temperature, which could be controlled by a heater and a thermometer at the evaporation cup, was about 50 K. No significant increase of attenuation was observed during condensation. This indicates that the film grew homogeneously at least on a scale of several hundred nanometers. Gas mixtures were prepared at room temperature in different concentrations by opening a valve between two identical gas storage volumes containing the pure gases at well-defined pressures. After a waiting time sufficiently long to allow complete mixing of the two components the gas was fed into the condensation capillary.

The desorption behavior was investigated by warming up the films at a constant heating rate of typically 2 K/h. Sublimation of condensed atoms leads to an increase of the sound velocity. During desorption the surrounding cold walls act as a very efficient cryopump for the evaporating

0031-9007/02/88(1)/016104(4)$15.00

atoms so that readsorption on the SAW device cannot occur.

Figure 1 shows the result of a typical desorption experiment on a quench-condensed pure Ne film. The initial rise of temperature from 1 to almost 8 K within some hours led on the scale of Fig. 1 only to very small changes of sound velocity. However, above 8 K the frequency starts to increase strongly due to the loss of film material. At 8.5 K the frequency change stops as the complete Ne film is desorbed and the SAW device is uncovered again. The sublimation process of a pure Ar film takes place in an entirely analogous way and is plotted in Fig. 1 against the top scale. The desorption threshold is shifted to ~30 K due to the higher binding energy of Ar. Since the atomic mass of Ar is about twice the mass of Ne, the increase of sound velocity due to desorbing Ar atoms is twice as large as for the same number of evaporating Ne atoms. Accordingly, in Fig. 1 the Ne film was considerably thicker than the Ar film.

When a binary mixture of Ar and Ne desorbs one might expect that either both species sublimate separately at their desorption temperature or that—in a random mixture—Ne sublimates almost continuously over a wide temperature range as the number of neighboring Ar atoms and hence the effective binding energy of the Ne atoms may strongly vary. The upper panel of Fig. 2 shows the desorption behavior of an $\text{Ar}_{56}/\text{Ne}_{44}$ mixture. In marked contrast to expectation, the relative change of sound velocity shows three characteristic steps at 8, 20, and 30 K and remains almost constant between these threshold temperatures. At 32 K the desorption process is finished. Since the sublimation temperatures of pure Ne and Ar are well known the first and last step can be assigned to the desorption of Ne and Ar, respectively. The nature of the step at 20 K can be deduced by comparison of the three step heights with the total amounts of Ne and Ar fed into the cryostat during initial film growth: The sum of the frequency shifts of the first two steps is almost half the shift of the final Ar desorption step at 30 K. Taking into account the mass ratio $m_{\text{Ar}} = 2m_{\text{Ne}}$ and the composition of the initial gas mixture, which was close to a ratio of 1:1, one is led to conclude that the second step at 20 K must be due to desorption of Ne.

For a closer analysis of this phenomenon we varied the Ne concentration of the quench-condensed binary mixtures. The lower panel in Fig. 2 shows a comparison of three mixtures with different $c_{\text{Ne}}$. All three films show the typical signature of $\delta f/f$: Two Ne steps at 8 and ~20 K and the desorption of Ar at 30 K. However, there are large quantitative differences: For $c_{\text{Ne}} = 84\%$ almost all Ne atoms desorb at 8 K and only a very small percentage of Ne at 20 K. For the second film with nearly similar concentration of Ar and Ne the steps at 8 and 20 K are of almost equal height while the behavior of the last film ($c_{\text{Ne}} = 28\%$) is quite the contrary to the first one as most Ne atoms desorb above 20 K and only very few at 8 K.

The investigation of additional desorption processes of Ar/Ne mixtures with different concentrations allows one to deduce a systematic behavior which can best be analyzed using the ratios:

$$\frac{\text{Ne}_{20\text{ K}}}{\text{Ne}_{\text{tot}}} := \frac{\text{No. of Ne atoms desorbing at } T \approx 20\text{ K}}{\text{Total number of Ne atoms}},$$

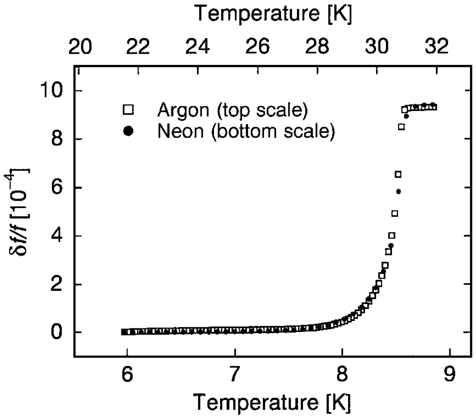

FIG. 1. Relative change of sound velocity during desorption of a pure neon (bottom axis) and a pure argon (top axis) film, respectively. The scaling factor between top and bottom axes is 3.6 corresponding to the ratio of the desorption thresholds of argon and neon. The heating rate was 2 K/h for both films.

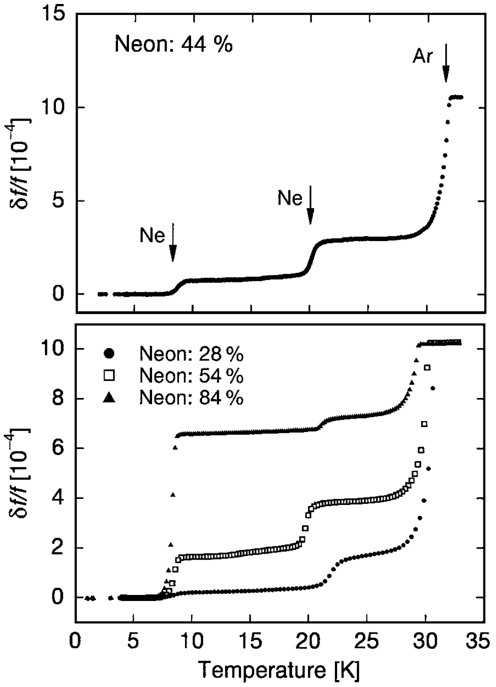

FIG. 2. Upper panel: desorption behavior of an $\text{Ar}_{56}/\text{Ne}_{44}$ mixture. Lower panel: desorption behavior of Ar/Ne films with different concentrations. For a better comparison all curves have been scaled to a total frequency change of $\delta f/f = 10^{-3}$. The scaling factors are 0.97 ($c_{\text{Ne}} = 28\%$), 1.03 ($c_{\text{Ne}} = 54\%$), and 1.07 ($c_{\text{Ne}} = 84\%$). The heating rate was 2 K/h for all films.

$$\frac{\mathrm{Ar}}{\mathrm{Ne}_{20\,\mathrm{K}}} := \frac{\text{Total number of Ar atoms}}{\text{No. of Ne atoms desorbing at } T \approx 20\text{ K}}.$$

Figure 3 shows the ratio $\mathrm{Ne}_{20\,\mathrm{K}}/\mathrm{Ne}_{\mathrm{tot}}$ as a function of $c_{\mathrm{Ne}}$. For large Ne concentration the desorption of Ne atoms occurs mainly at 8 K. At smaller concentration an increasing number of Ne atoms remain in the film up to 20 K. Figure 4 shows the ratio $\mathrm{Ar}/\mathrm{Ne}_{20\,\mathrm{K}}$ as a function of $c_{\mathrm{Ne}}$. For small and large $c_{\mathrm{Ne}}$ one finds $\mathrm{Ar}/\mathrm{Ne}_{20\,\mathrm{K}} \approx 3{:}1$; for medium concentrations the ratio is close to 2:1. We come back to this point further below.

To explain this remarkable desorption behavior we emphasize again that according to thermodynamical equilibrium conditions the system Ar/Ne should tend to phase separation. Although our experimental arrangement leads to film configurations far away from equilibrium, the two discrete temperatures of Ne desorption indicate the existence of two different phases. Since the first temperature is identical with the desorption temperature of pure Ne we suggest that at $T = 8$ K Ne atoms desorb from a phase of pure Ne.

The second step at 20 K indicates a considerably higher effective binding energy $\epsilon_{\mathrm{eff}}$ of the Ne atoms which must arise from the presence of Ar atoms. This binding energy appears to be well defined as the second step is not broader than the steps at 8 and 30 K. Using the Lorentz-Berthelot rule for binary Lennard-Jones mixtures $\epsilon_{AB} = \sqrt{\epsilon_{AA}\epsilon_{BB}}$ it is possible to estimate the binding energy for Ar/Ne. The resulting value is 80% higher than for the Ne/Ne bond. However, the temperature of the second Ne desorption is about 150% higher than the desorption temperature of pure Ne. This indicates that the number of Ar next neighbors exceeds the number of Ne next neighbors. The ratio $\mathrm{Ar}/\mathrm{Ne}_{20\,\mathrm{K}}$ plotted in Fig. 4 as a function of neon concentration confirms this assumption. We suggest that these films form a metastable phase with a regular stoichiometric configuration of the two atomic species. About 20 K this phase is destroyed and Ne can desorb. The Ar atoms remain on the substrate and do not evaporate below 30 K.

A more accurate analysis of the position of the second desorption step (see, e.g., Fig. 2) reveals an interesting correlation with the data of Fig. 4: For Ne concentrations close to 50% the ratio $\mathrm{Ar}/\mathrm{Ne}_{20\,\mathrm{K}}$ is ~2:1 and the desorption temperature ~20 K. For small and large Ne concentrations where the ratio $\mathrm{Ar}/\mathrm{Ne}_{20\,\mathrm{K}}$ is ~3:1, the desorption temperature is almost two Kelvin higher. The observed positions of the second step are in excellent agreement with a plausible extension of the Lorentz-Berthelot rule, namely, $T_{\mathrm{Ar_2Ne}} \simeq (T_{\mathrm{Ar}}^2 T_{\mathrm{Ne}})^{1/3}$ and $T_{\mathrm{Ar_3Ne}} \simeq (T_{\mathrm{Ar}}^3 T_{\mathrm{Ne}})^{1/4}$, where the $T_i$ denote the desorption thresholds of the different films.

To the best of our knowledge there are no publications reporting on the existence of a stable $AB_3$ structure. At thermodynamical equilibrium and for size ratios $0.42 < \alpha < 0.62$ a stable crystalline structure of the form $AB_2$ should exist in combination with a pure phase of $A$ or $B$ [1,12]. The size ratio of the system Ar/Ne, however, is far beyond the upper limit of this region. Nevertheless, our results clearly indicate the presence of $AB_2$ and $AB_3$ phases although these are only metastable. We assume that the initial preparation in an extreme nonequilibrium state allows the films upon annealing to enter metastable phases which are energetically only slightly unfavorable compared to the true equilibrium configuration. If the energy barrier to enter the equilibrium state is sufficiently high the metastable phases may exist over a wide temperature range. The formation of different phases in binary Lennard-Jones mixtures turns out to be a very subtle and complex matter; at present it is entirely unclear why an $\mathrm{Ar_2Ne}$ phase emerges for medium concentrations and $\mathrm{Ar_3Ne}$—although according to equilibrium considerations less favorable—for small and large Ne concentrations. Moreover, we found very recently that additional metastable phases may occur when the temperature of quench condensation is raised above 2 K: The desorption step at 8 K almost vanishes and a new step at 12.5 K comes up. Using again the extended

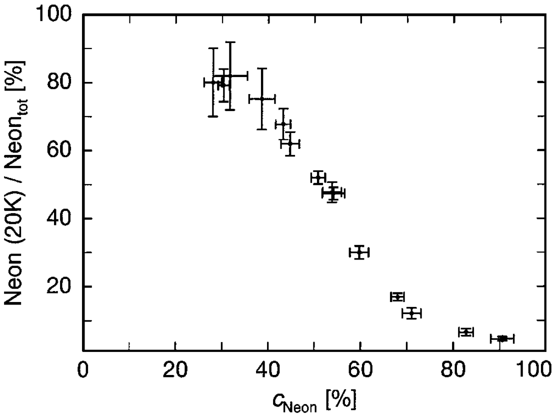

FIG. 3. Portion of neon atoms desorbing at 20 K as a function of neon concentration.

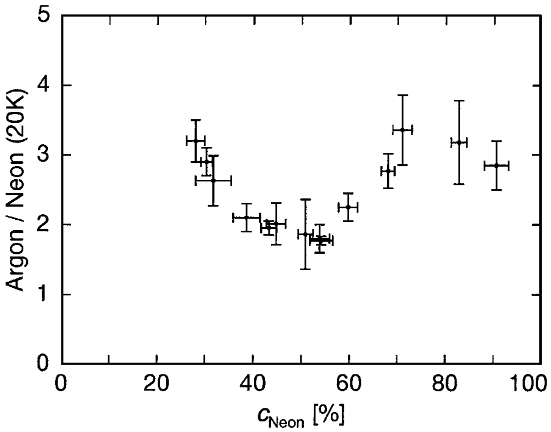

FIG. 4. Ratio of argon atoms (desorbing at 30 K) and neon atoms desorbing at 20 K as a function of neon concentration.

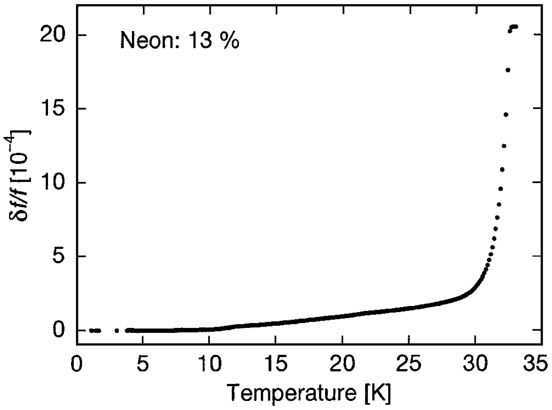

FIG. 5. Relative frequency change during desorption of an Ar/Ne mixture with a neon concentration of 13%. The same qualitative behavior was observed for all neon concentrations smaller than 25%. The heating rate was 6 K/h.

Lorentz-Berthelot rule this temperature would be fully consistent with the formation of an $ArNe_2$ phase [24].

In Figs. 3 and 4 no data are shown for concentrations smaller than $c_{Ne} < 25\%$ and larger than $c_{Ne} > 92\%$. In Fig. 5 we show an example of a film with a Ne concentration of only 13%. Above 10 K the frequency starts to rise nearly continuously until above 30 K a strong frequency shift occurs. There is no further step either at 8 K or at 20 K. In such mixtures with $c_{Ne} < 25\%$ no phase separation seems to occur and no ordered $AB_2$ or $AB_3$ structures are developed. Instead, on annealing a substitutionally disordered solid is formed. For small $c_{Ne}$ the Ne atoms behave like impurity atoms in an Ar film. The number of Ar next neighbors determines the binding energy. Corresponding to this widely distributed energy the individual Ne atoms evaporate nearly continuously over a broad range of temperatures.

At concentrations $c_{Ne} > 92\%$ yet another sublimation behavior is found. There is only a large frequency shift at 8 K and a smaller step at 30 K. Between these temperatures the sound velocity remains nearly constant and, in particular, there is no step at 20 K. Both rare gases desorb separately at the corresponding sublimation temperatures, in complete analogy to the desorption behavior of $Xe_{90}Ar_{10}$ [22]. At present an unambiguous interpretation of these data is hardly possible. It may be that the films are substitutionally disordered and that the desorption of Ne is barely hindered by the presence of only very few Ar atoms. However, the data are also consistent with the alternative interpretation of a complete phase separation into two phases of pure Ar and pure Ne.

To summarize, we have found a remarkably complex desorption behavior of binary mixtures of Ar and Ne. The initial disorder due to quench condensation at 1 K seems to play a crucial role for the existence of metastable phases even at subsequent annealing stages up to 20 K. Future investigations will include mixtures with different noble gases (krypton, xenon) and a careful analysis of the influence of the condensation temperature on the occurrence of various metastable phases.

Valuable discussions with R. Kühn are gratefully acknowledged. This work was supported by the Deutsche Forschungsgemeinschaft (Grant No. Hu359/10).

[1] X. Cottin, J. Chem. Phys. **99**, 8914 (1993).
[2] J. L. Barrat, M. Baus, and J. P. Hansen, J. Phys. C **20**, 1413 (1987).
[3] D. Frenkel and A. J. C. Ladd, J. Chem. Phys. **81**, 3188 (1984).
[4] X. Cottin and P. A. Monson, J. Chem. Phys. **105**, 10 022 (1996).
[5] S. W. Rick and A. D. J. Haymet, J. Chem. Phys. **90**, 1188 (1989).
[6] M. J. Murray and J. V. Sanders, Philos. Mag. A **42**, 721 (1980).
[7] M. J. Vlot and J. C. van Miltenburg, H. A. J. Oonk, and J. P. van der Eerden, J. Chem. Phys. **107**, 4345 (1997).
[8] M. R. Hitchcock and C. K. Hall, J. Chem. Phys. **110**, 11 433 (1999).
[9] W. G. T. Kranendonk and D. Frenkel, Mol. Phys. **72**, 679 (1991).
[10] M. D. Eldridge, P. A. Madden, and D. Frenkel, Mol. Phys. **79**, 105 (1993).
[11] M. D. Eldridge, P. A. Madden, and D. Frenkel, Mol. Phys. **80**, 987 (1993).
[12] M. D. Eldridge, P. A. Madden, and D. Frenkel, Nature (London) **356**, 35 (1993).
[13] P. Bartlett, R. H. Ottewill, and P. N. Pusey, Phys. Rev. Lett. **68**, 3801 (1992).
[14] A. E. Curzon and A. T. Pawlowicz, Proc. Phys. Soc. London **85**, 375 (1965).
[15] K. Müller, J. Appl. Phys. **62**, 1796 (1987).
[16] X. W. Zhou, R. A. Johnson, and H. N. G. Wadley, Acta. Mater. **45**, 1513 (1997).
[17] K. Müller, J. Vac. Sci. Technol. A **3**, 2089 (1985).
[18] W. Schulze, H. U. Becker, and H. Abe, Ber. Bunsen-Ges. Phys. Chem. **82**, 257 (1978).
[19] L. Sanche, G. Perluzzo, G. Bader, and L. G. Caron, J. Phys. Chem. **77**, 3285 (1982).
[20] H. Menges and H. von Löhneysen, J. Low Temp. Phys. **84**, 237 (1991).
[21] M. Schneider, A. Rahman, and I. K. Schuller, Phys. Rev. Lett. **55**, 604 (1985).
[22] M. Loistl and F. Baumann, Z. Phys. B **82**, 199 (1991).
[23] B. A. Auld, *Acoustic Fields and Waves in Solids* (Robert E. Krieger, Malabar, FL, 1990), 2nd ed., Vol. 2.
[24] J. Meier, M. Heitz, M. Layer, J. Classen, and S. Hunklinger (to be published).