

Structural peculiarities of quench-condensed pure and argon-doped nitrous oxide

A.A. Solodovnik and V.V. Danchuk

B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47 Lenin Ave., Kharkov 61103, Ukraine
solodovnik@ilt.khakov.ua

Electron diffraction studies have been carried out for condensed N_2O and N_2O -Ar films. Deposition took place at substrate temperatures of 10 and 20 K. The growth process of N_2O deposits was studied. A strong effect of argon impurities on the structure of the nitrous oxide matrix has been observed. The phase separation of the solutions was studied. The equilibrium solubility of argon atoms in nitrous oxide is very low. Introduction of a small amount of argon impurity into the molecular lattice destroyed the crystal structure. An effect of the size of the sample on its structure was also studied.

PACS: 67.80.Cx

Introduction

Solid nitrous oxide belongs to the class of molecular cryocrystals consisting of linear molecules. At low temperature the symmetry of this crystal is described by the $Pa3$ space group in which the centers of mass of the molecules are localized at the sites of the fcc lattice and the axes of the molecules are directed along the four cube diagonals [1,2]. The strong anisotropic interaction between triatomic molecules (as both «long» N_2O and CO_2) stabilizes the state with orientational order up to the triple point. Doping of the ordered modification with atomic («rotationally neutral») impurities could lead to realization of phase transitions due to the molecule disorientation and the formation of an orientational glass state [3,4]. The number of transformations can be still greater in the case of small objects. Change in the structure of deposited particles can also be caused by the size factor. One can assume that the existence of an anisotropic interaction may also affect the character of a dimensional phase transition. The possible formation of icosahedral CO_2 clusters was considered in [5]. According to the experimental data [6] the CO_2 free clusters had the structure inherent to the bulk crystal. However the authors observed an intensification of the librational motion of the CO_2 molecules in small crystalline clusters. Investigation of the initial stage of sample preparation is important for understanding

the mechanism of the crystalline phase formation in pure solids and solutions.

The effect of dilution of spherically symmetric atoms in a molecular crystal matrix on the orientational order has been investigated in CO_2 -Ar alloys [3,7]. It was established that the rare-gas doping lowers the potential barrier hindering the rotation of molecules. As a result, the orientational ordering factor of CO_2 molecules decreases considerably with increasing Ar concentration. The nearest analog of solid carbon dioxide is solid nitrous oxide. As a molecule, N_2O is physically very similar to CO_2 , except for its dipole moment. In the case of nitrous oxide a phase transition attributed to dipole ordering may occur at $T < 11$ K [8]. However according to the structure study [9] the «head-to-tail» order is absent in nitrous oxide condensates down to 2.2 K. A partial dipolar ordering reveals itself in peculiarities of the temperature dependence of the Grüneisen constant for solid N_2O [10].

Experimental

Investigations were carried out by the transmission electron diffraction technique using a helium cryostat [11,12]. Measurements were made in the temperature range between 6 and 60 K. Samples were prepared *in situ* by depositing gaseous mixtures on a polycrystalline Al substrate film at various temperatures. CO_2 [13] and N_2O [14] samples quench-deposited under certain conditions may be amorphous. Our experi-

ments also enabled us to establish conditions for the formation of a stable $Pa\bar{3}$ structure. We used 99.99 % pure gas to make the deposits. The concentration of the gaseous phase was determined by measuring the partial pressure of components with the help of a sensitive manometer. The Al film also served as the internal standard. The absolute error in determining the lattice parameter for high-intensity sharp peaks usually did not exceed 0.005 Å. For weak and highly blurred reflection, the error was twice as large. The samples did not reveal any noticeable signs of texture. The effective thickness of the samples ranged from 2 to 45 nm. As the procedure was capable of detecting a new phase if the dimensions of its domains were of the order of few nanometers, diffraction patterns were recorded continuously during the condensation.

Results and discussion

Pure nitrous oxide

We present a detailed study of a growth process of N_2O crystalline deposits in the temperature range 6–20 K. The structure of N_2O samples was investigated as a function of both the temperature of the substrate and the dimensional factor at the chosen condi-

tions. The sequence of changes in the diffraction patterns during deposition at 10 K is shown in Fig. 1. The indices of the peaks are marked on top; $S = 4\sin \theta/\lambda$ is the diffraction vector modulus, θ is the Bragg angle, and λ is the electron wavelength. At the initial stage of the condensation we observed the appearance aggregates having a structure with complete vanishing of reflections caused by the orientational ordering of the molecular axes (see Fig. 1,*a*). «Superstructural» peaks such as (210), (320), (321) were absent. The diffraction pattern obtained can be interpreted as that of an fcc structure. This will be discussed later. With further increase in the amount of deposited gas a transition of the crystalline phase into an amorphous one was observed (see Fig. 1,*b*). The diffraction pattern of the condensate showed one broad, diffuse diffraction ring at the position where the (111) and (200) reflections are expected to occur. As the molecular aggregates became larger, the nature of the intensity distribution of the diffraction pattern changed. The amorphous modification transformed into an ordered phase (see Fig. 1,*c*). All of the diffraction peaks correspond to the $Pa\bar{3}$ structure. This is indicated by a sharpening of the (111) and (200) peaks and the appearance of the (210) maxima inherent to the long-range-ordered phase. No change in intensity

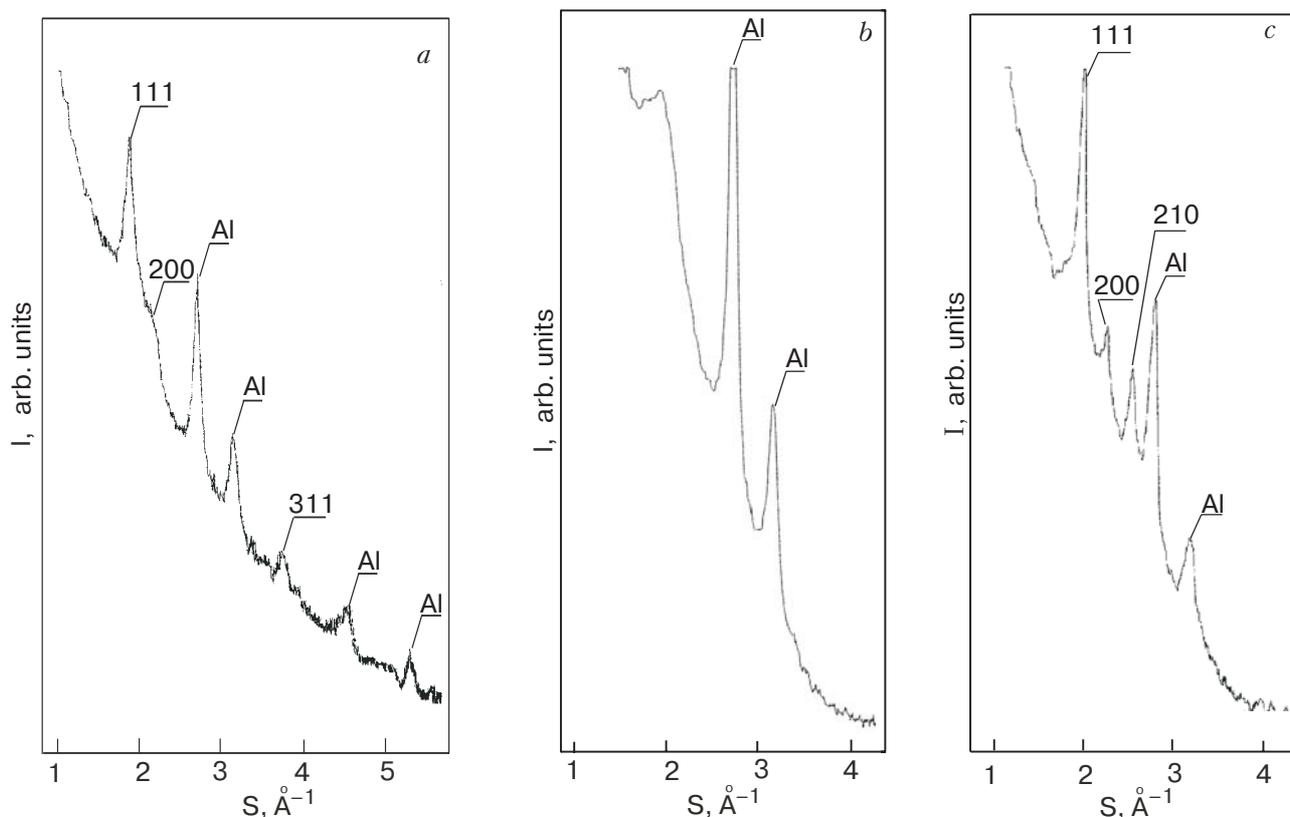


Fig. 1. Intensity distribution corresponding to the electron diffraction pattern from N_2O samples. The evolving structure during the growth process at 10 K. Time of quenching is 20 s. The initial stage of sample formation (*a*); time of quenching is 2 min, amorphous phase (*b*); time of quenching is 3.5 min, $Pa\bar{3}$ structure (*c*).

along the diffraction rings was observed. Precise measurements of the diameters of the diffraction rings and the corresponding calculations gave the following value of the lattice parameter of the ordered phase: $a = (5.666 \pm 0.005) \text{ \AA}$. As indicated above, the structure of the initial deposit corresponds to the fcc phase. The evidence for this conclusion is the absence of «superstructural» reflections and the presence of the (311) peak, which is very weak in $Pa\bar{3}$ group symmetry. The value of lattice parameter of the fcc phase is $a = 5.682 \text{ \AA}$. One can see that the difference between the values of the lattice parameter of the both phases is not big. However, it is known that disordering of the linear molecules leads to an increase of the lattice parameter. On other hand, a linear decrease in the value of the lattice parameter with decreasing cluster size was observed. The contraction from the bulk solid is about 0,35% for a small CO_2 cluster [6]. This contradiction can be explained using a simple model to account for the linear variation. The clusters have the form of isotropic spheres with compressibility and surface stress, producing an effective internal pressure. The contradiction of the lattice parameter and the character of the intensity distribution [15] (see Fig. 1,*a*) permit us to suggest such an explanation. At the initial stage of growth we obtain a noncrystalline phase, as can be seen from the diffraction pattern (see Fig. 1,*a*). The (111) reflection is sharp, but differs from the line profile of ideal crystals by a strong broadening of the line base. The (200) reflection is broad and diffuse and not distinctly separated from (111) [15]. During the growth process the dimensions of the sample increase from 2 to 45 nm. The most interesting result is the nitrous oxide solid with a structure in which the ordered arrangement of N_2O molecules is absent.

At 20 K diffraction peaks appeared at the positions corresponding to the $Pa\bar{3}$ structure during quenching pure nitrous oxide (see Fig. 2). Reflections (200) and (210) were weak. However with increasing size of a sample all the peaks of $Pa\bar{3}$ symmetry were clearly manifested.

Nitrous oxide doped with argon

The choice of the N_2O -Ar system is dictated by the following circumstance. To our knowledge no data are available in the literature about the character of the phase diagram of these components. Nitrous oxide-based solutions are such systems in which the molecular component does not exhibit a transition from an orientationally ordered to a disordered phase in the solid state. The choice of argon as the dopant is motivated mainly by the considerable difference in the molar volumes. The volume difference is 7%. This fact al-

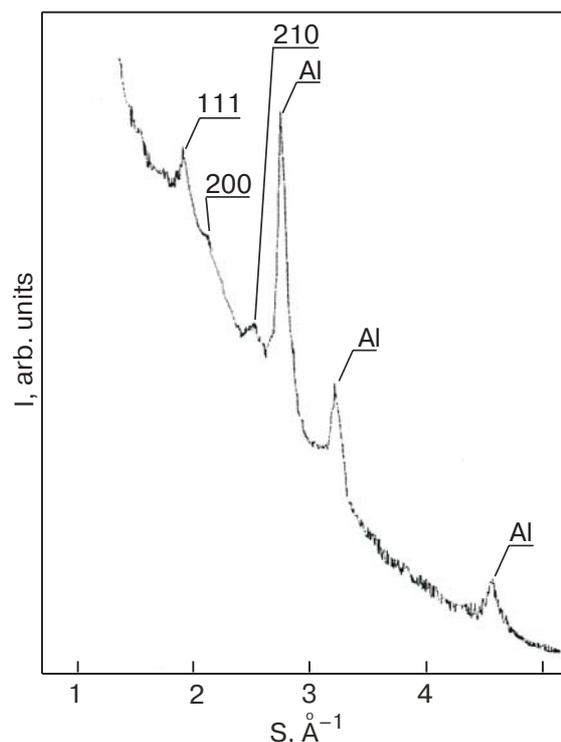


Fig. 2. Intensity distribution corresponding to the electron diffraction pattern from N_2O samples at the initial stage of formation at 20 K. Time of quenching is 20 s.

lows us to expect interesting results. At first we present the results of the investigation of large N_2O -Ar aggregations. The aim is to obtain information about the solubility of argon in the nitrous oxide matrix and to establish the crystallographic structure of the solid solutions.

The solidified N_2O -Ar mixtures were prepared at 20 K and were recorded. We illustrate the effect of Ar doping (see Fig. 3,*a*). If the argon concentration did not exceed 3.5 mol.% the electron diffraction patterns displayed the bright halo and very weak peaks of the N_2O ordered phase. The center of the halo coincides with the (111) reflection. The presence of the peaks (200) and (210) confirms the weak degree of ordered arrangement of the N_2O molecules. For argon fractions of about 10 mol. % one can observe the beginning of a phase separation process. The character of diffraction patterns evidenced the decomposition of the solutions. In this case there are two systems of diffraction rings. One of these corresponds to the N_2O ultradisperse phase, while the other, which contains peaks of much lower intensity, corresponds to the Ar fcc modification (see Fig. 3,*b*). With increasing argon content in the mixture the intensity of the Ar peaks increases. On heating the samples up to 30 K the patterns changed quickly: the halo disappeared and sharp rings appeared, the positions of which corresponded to

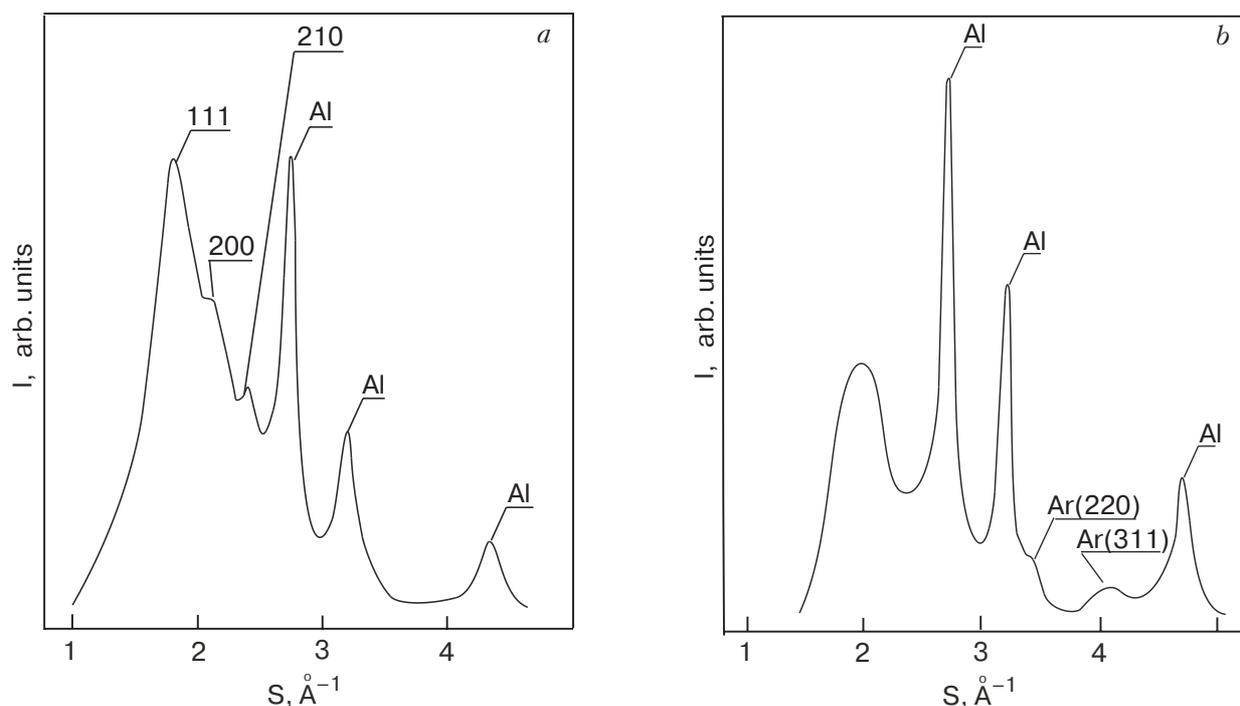


Fig. 3. The diffraction pattern of N_2O -3.5% Ar (a) deposited at 20 K and N_2O -10% Ar (b) deposited at 20 K.

those of the diffraction peaks from the N_2O ordered phase. Annealing above 30 K was accompanied by intense evaporation of argon. The desorption of argon made it possible to form the $Pa3$ structure of nitrous oxide. According to our measurements, the equilibrium solubility of argon atoms in the N_2O matrix is very low. The structure of the nitrous oxide lattice is very sensitive to the concentration of impurities. The introduction of a small amount of argon into the molecular lattice led to destruction of the crystal structure.

Acknowledgment

The authors wish to express thanks to M. A. Strzhemechny for stimulating discussions and substantial support.

1. L. Vegard, *J. Phys.* **71**, 465 (1932).
2. W.C. Hamilton and M. Petrie, *J. Phys. Chem.* **65**, 1453 (1953).
3. M.A. Strzhemechny, A.A. Solodovnik, and S.I. Kovalenko, *Fiz. Nizk. Temp.* **24**, 889 (1998) [*Low Temp. Phys.* **24**, 669 (1998)].
4. V.A. Hochli, K. Knor, and A. Loidl, *Adv. Phys.* **39**, 408 (1990).
5. B.W. van de Waal, *J. Chem. Phys.* **79**, 3948 (1983).
6. G. Torchet, H. Bouchier, J. Farges, M.F. de Feraudy, and B. Raoult, *J. Chem. Phys.* **81**, 2137 (1984).
7. A.A. Solodovnik, M.A. Strzhemechny, S.I. Kovalenko, *Czech. J. Phys.* **46**, 521 (1996).
8. M.W. Melhuish and R.L. Scott, *J. Phys. Chem.* **68**, 2301 (1964).
9. S.I. Kovalenko, E.I. Indan, A.A. Khudoteplaya, and Y.N. Krupskii, *Phys. Status Solidi A* **20**, 629 (1973).
10. A.M. Tolkachev, V.G. Manzhelii, V.P. Azarenkov, A. Jezowski, and E.A. Kosobutskaya, *Fiz. Nizk. Temp.* **6**, 1533 (1980) [*Sov. J. Low Temp. Phys.* **6**, 747, (1980)].
11. S.I. Kovalenko and V.A. Godovanyi, *Prib. Tekh. Eksp.* **2**, 235 (1967).
12. S.I. Kovalenko and A.A. Solodovnik, *Fiz. Nizk. Temp.* **18**, 889 (1992) [*Sov. J. Low Temp. Phys.* **18**, 626 (1992)].
13. M. Falk, *J. Chem. Phys.* **86**, 560 (1987).
14. N.V. Krainykova and M.A. Strzhemechny, *Fiz. Nizk. Temp.* **21**, 1254 (1995) [*Low Temp. Phys.*, **21**, 1254 (1995)].
15. J.W. Lee and G.D. Stein, *Surf. Sci.* **156**, 112 (1985).