

# Structural-phase transitions in solid nitrous oxide

A. Drobyshev, A. Aldiyarov, E. Korshikov, D. Sokolov, and V. Kurnosov

Citation: Low Temp. Phys. 38, 1058 (2012); doi: 10.1063/1.4765095 View online: http://dx.doi.org/10.1063/1.4765095 View Table of Contents: http://ltp.aip.org/resource/1/LTPHEG/v38/i11 Published by the American Institute of Physics.

# **Related Articles**

Structure and phase transitions in 0.5(Ba0.7Ca0.3TiO3)-0.5(BaZr0.2Ti0.8O3) from -100°C to 150°C J. Appl. Phys. 113, 014103 (2013)

Ice polyamorphism in the minimal Mercedes-Benz model of water J. Chem. Phys. 137, 244503 (2012)

Transformation volume strain in Ni-Mn-Ga thin films Appl. Phys. Lett. 101, 241912 (2012)

Phase transformation in hexagonal ErMnO3 under high pressure J. Appl. Phys. 112, 113512 (2012)

Electric field-induced tetragonal to orthorhombic phase transitions in [110]c-oriented BaTiO3 single crystals Appl. Phys. Lett. 101, 232904 (2012)

## Additional information on Low Temp. Phys.

Journal Homepage: http://ltp.aip.org/ Journal Information: http://ltp.aip.org/about/about the journal Top downloads: http://ltp.aip.org/features/most\_downloaded Information for Authors: http://ltp.aip.org/authors

## **ADVERTISEMENT**



Downloaded 15 Jan 2013 to 155.198.227.10. Redistribution subject to AIP license or copyright; see http://ltp.aip.org/about/rights\_and\_permissions

## Structural-phase transitions in solid nitrous oxide

A. Drobyshev,<sup>a)</sup> A. Aldiyarov, E. Korshikov, D. Sokolov, and V. Kurnosov

*Al-Farabi Kazakh National University, Almaty, Kazakhstan* (Submitted July 9, 2012) Fiz. Nizk. Temp. **38**, 1340–1346 (November 2012)

Features of the transformations in cryocondensed samples of nitrous oxide under thermal cycling at temperatures near T = 40 K are studied. It is shown how the deformation and translational vibrational subsystems of the condensed state of nitrous oxide react to these transitions. Measured vibrational spectra of the samples and the amplitudes and positions of the absorption bands of the characteristic vibrations are used to determine the temperature and character of the thermally stimulated transitions in films of cryocondensed nitrous oxide. An analysis of these IR spectra indicates that the transition from the amorphous state of nitrous oxide to the crystalline state takes place in several stages that reflect the relaxation processes associated with particular vibrational modes of the nitrous oxide molecule. The differences in the transition temperatures are determined by the activation energies characteristic of these modes. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4765095]

#### 1. Introduction

The unusual properties of nitrous oxide, in particular the polymorphism of its solid phase at low temperatures, have long drawn the attention of researchers.<sup>1–3</sup> Our laboratory has also played a part in this area. In particular, some interesting experimental data were obtained in 1988.<sup>4,5</sup> The rate of condensation of solid nitrous oxide was being studied as a function of the pressure of the gaseous phase and the temperature of the substrate. It was found that the cryodeposition process is accompanied by the emission of visible electromagnetic radiation, which was a direct consequence of the gas-solid phase transition (Fig. 1). A time scan of a single pulse is shown in Fig. 1(b). It is clear that the risetime of the emission is no more than 30 ms.

The spectral composition of the cryoemission has been studied<sup>6</sup> and a typical spectrum of this emission is shown in Fig. 2. The emission spectrum contains two distinct maxima. The first and most distinct, lies at wavelengths of 320-400 nm. The second peak is observed at longer wavelengths and has a maximum at 700 nm.

IR spectrometric studies of the state of cryocondensed films of nitrous oxide have been conducted at temperatures ranging from 12 K to the sublimation temperature.<sup>7,8</sup> The N<sub>2</sub>O cryocondensate was deposited at T = 12 K and subjected to slow warming. It was found that around 40 K the state of the sample underwent a sudden change which showed up as a change in the position and shape of the characteristic bands in the IR spectra (Fig. 3(a)). Warming of the film with the frequency of the spectrometer fixed made it possible to determine the temperature interval for the transition more accurately (Fig. 3(b)). Later electron diffraction studies of this phenomenon<sup>9,10</sup> showed that a sample condensed at T = 12 K is in an amorphous state. During warming to 40 K it undergoes a transition to a crystalline state with a cubic lattice.

Despite rather wide ranging studies, the mechanism of these transitions is still unknown. In the meantime, in recent years a number of papers that are thematically related to our work<sup>11–13</sup> have been published, so it is possible to examine

this problem from another point of view. We have carried out the studies described in this article in order to obtain additional information.

### 2. An idea and an experiment

Results from a study of the features of the transformations in cryocondensed samples of nitrous oxide during thermal cycling at temperatures around T = 40 K are presented here. The goal of these studies was to clarify how the deformation and translational vibrational subsystems of the condensed state of nitrous oxide react to these transitions. In other words, is this transformation one that simultaneously affects all the degrees of freedom of the nitrous oxide molecule, or is there a set of successive transitions corresponding to one or another type of vibrations of the molecule. Observations were made in the neighborhoods of fundamental vibrational frequencies of the nitrous oxide molecule:<sup>14–17</sup>

 $\nu_1 = 1284.91 \text{ cm}^{-1}$ , longitudinal asymmetric vibrations of the molecule (100–00<sup>0</sup>0);

 $\nu_2 = 588.77 \text{ cm}^{-1}$ , transverse deformational vibrations of the molecule (01<sup>1</sup>0-00<sup>0</sup>0); and

 $\nu_3 = 2223.76 \text{ cm}^{-1}$ , longitudinal symmetric vibrations of the molecule (001–00<sup>0</sup>0).

We have described the apparatus and techniques for the measurements several times before.<sup>18,19</sup> The major difference from the earlier studies of nitrous oxide is a combination of optical and thermal desorption methods, which has made it possible to obtain information simultaneously from two independent bases of experimental data. We have used this approach successfully in an earlier study of structural phase transitions in cryocondensates of water and ethanol.<sup>20,21</sup>

Here the object of study was films of cryovacuum condensates of nitrous oxide produced under the following conditions: the condensation surface is a silvered copper mirror substrate with a diameter of 40 mm; the sample condensation temperature is  $T_c = 16$  K; the pressure of the gaseous phase during condensation is  $P = 10^{-3}$  Pa; the sample thickness is

1058



FIG. 1. Emission during cryodeposition of nitrous oxide. The condensation temperature is 100 K and the gas pressure in the vacuum vessel is 50 Pa. (a) Curve 1 is the signal from the laser interferometer with detection of individual emission bursts. Curve 2 shows the bursts without the laser. 3 and 4 indicate the luminosity of the sample with heating above 130 K. (b) Time scan of a single pulse.

 $d = 2 \mu m$ ; the rate at which the samples are heated is t = 1 K/min; and, the purity of the gaseous phase nitrous oxide is 99.92%. By measuring the vibrational spectra of the samples and identifying the change in amplitude and position of the absorption band for the characteristic vibrations, it is possible to determine the temperature and character of the ther-





FIG. 2. A typical spectrum of cryocondensate emission (curve 1).<sup>9</sup> Curve 2 is a reference signal from calibration filters.

mally stimulated transformations in the cryocondensate films of nitrous oxide.

The experiments are conducted in the following order: first, the vacuum chamber was pumped down to a pressure of  $2 \cdot 10^{-5}$  Pa, after which the substrate was cooled to T = 16 K. Gaseous nitrous oxide is released into the vessel through a leak valve to the specified condensation pressure  $(10^{-3} \text{ Pa})$ . A film of cryocondensate developed on the substrate surface; its rate of growth and refractive index were measured with a two-beam laser interferometer. When the required thickness was reached, the gas feed was turned off and the IR spectra of the samples were measured over frequencies of  $400-4200 \text{ cm}^{-1}$  for 5-10 min. Then the frequency of the IR spectrometer was set at the value corresponding to the type of molecular vibrations to be analyzed. After this, the sample was slowly warmed with simultaneous recording of the spectrometer signal at the chosen observation frequency. The pressure of the gaseous phase in the vacuum vessel was also measured. Here it was kept in mind that the structural transformations in the sample lead to desorption from it of impurities (nitrogen) that had been captured during cryocondensation and to a corresponding

FIG. 3. IR spectrometric studies of transitions in nitrous oxide cryocondensates.<sup>11</sup> (a) The change in the position of the absorption band of the deformation vibrations of the nitrous oxide molecule resulting from an increase in the temperature from 16 to 45 K. (b) The change in the IR spectrometer signal at 585 cm<sup>-1</sup> as the sample temperature is raised. The condensation temperature is T = 16 K, the film thickness is  $d = 2.5 \,\mu$ m, and the heating rate is 1 K/ min.



FIG. 4. Effect of warming temperature of thin films of nitrous oxide films on the shape and position of the absorption bands corresponding to deformation and longitudinal vibrations of the N<sub>2</sub>O molecule. The spectra were obtained with a condensation temperature T = 16 K and after warming to T = 45 K. The lower parts of the graphs are thermograms of the change in the IR spectrometer signal at a fixed observation frequency. The film thicknesses are  $d = 2 \mu m$ .

increase in pressure, which provides additional information that is independent of optical measurements.

#### 3. Results

Figure 4 shows the results of a study of the influence of the warming temperature for thin cryocondensate films of nitrous oxide on the shape and position of the absorption bands corresponding to deformation and longitudinal vibrations of the N<sub>2</sub>O molecule. The spectra were taken at the condensation temperature T = 16 K and after heating to T = 45 K. The lower part of the figure shows thermograms of the change in the IR spectrometer signal during warming at fixed observation frequency.

These data show that there are number of features typical of the different types of vibrations and the spectra corresponding to them.

- 1. Frequencies of 560–600 cm<sup>-1</sup> corresponding to deformational vibrations. Warming the film leads to a significant narrowing of the absorption band and a corresponding shift to higher frequencies. Here the high frequency edge of the absorption band retains its position. The change in the frequency at the half width of the absorption is  $\Delta \nu = 1.3$  cm<sup>-1</sup>. There is a sudden change in the IR spectrometer signal at a frequency of  $\nu = 584$  cm<sup>-1</sup> within the temperature interval from 33.3 to 34 K.
- 2. Frequencies of 1200–1400 cm<sup>-1</sup> corresponding to longitudinal asymmetric vibrations. Heating the film leads to shift of the band as a whole to higher frequencies and a a reduction in the amplitude of the absorption. The change in the frequency at the absorption half width is  $\Delta \nu = 9.1$  cm<sup>-1</sup>. At  $\nu = 1280$  cm<sup>-1</sup>, a sudden change in the IR spectrometer signal was observed at temperatures within the interval 27.2–28.7 K.



FIG. 5. Thermally stimulated variations in the position of the low frequency boundary of the absorption band of the nitrous oxide molecule for deformation (a), and longitudinal asymmetric (b) and longitudinal symmetric (c), vibrations. The curves are shifted along the Y axis.



FIG. 6. Optical and thermal desorption data for studies of the structural transitions in cryovacuum condensates of nitrous oxide.

3. Frequencies of 2100–2300 cm<sup>-1</sup> corresponding to longitudinal symmetric vibrations. Heating the film from 16 to 45 K leads to a sharp reduction in the width of the absorption band with a shift to higher frequencies, as well as to a significant reduction in the amplitude of the absorption. The change in the frequency at the absorption half width is  $\Delta \nu = 13.1 \text{ cm}^{-1}$ . At  $\nu = 2224 \text{ cm}^{-1}$ , the transition takes place in two stages. A first sudden change in the signal is observed at temperatures within the interval 27.4–29.4 K. After that, over 29.5–35 K the signal remains relatively stable. A second, smoother transition takes place at 35–40.3 K.

An analysis of the data in Fig. 4 shows the following: the transition from an amorphous to a crystalline state of nitrous oxide takes place over several stages which reflect relaxation processes that correspond to specific vibrational modes of the nitrous oxide molecule. The differences in the temperatures of the transitions are determined by the characteristic activation energies of these vibrational modes. To study this phenomenon in more detail, we have measured the vibrational spectra of the warmed samples at fixed temperatures near the transition parameters. These spectra have been used to determine the position of the boundary of the absorption band at a fixed frequency as a function of the sample temperature. The data are shown in Fig. 5.

The curves of Fig. 5 have distinctive features which reflect the temperature dependence of the position of the absorption bands as a whole.

As the temperature is raised from T = 28 K, the deformation band begins to shift toward lower frequencies and reaches an extreme position at T = 33 K (the minimum in the



FIG. 7. An energy diagram of the isomorphic states of the nitrous oxide molecule (data from Ref. 25).



FIG. 8. Illustrating the shift of the absorption bands of the characteristic vibrations of nitrous oxide in the neighborhood of T = 40 K.

curves). Further increases in the temperature cause the absorption band to shift toward the "blue" and to become significantly narrower. The process is complete at 40 K.

The absorption band corresponding to longitudinal asymmetric vibrations also begins at T = 28 K. Initially it shifts to the "red," reaching a maximum shift at T = 33 K. Further temperature rises, as in the case of the deformation vibrations, lead to a shift of the band toward higher energies, with the shift reaching a maximum at T = 38 K.

The absorption band for the longitudinal symmetric vibrations (Fig. 5(c)) has a sharp "blue" shift at T = 28 K and reaches a maximum at T = 33 K. Then there is a sort of stabilization, and at T = 38 K, yet another shift which finishes at T = 40 K.

It should be noted that the measurement data shown in Figs. 4 and 5 can only be compared somewhat arbitrarily, since they correspond to different heating conditions: continuous (Fig. 4) and stepwise (Fig. 5). Nevertheless, the characteristic features and temperature boundaries are intrinsic to the observed processes in both cases.

We have used thermally stimulated desorption<sup>22,23</sup> as a nonoptical method for detecting structural transitions in solid nitrous oxide. The results of the thermal desorption measurements (upper curves) are compared with the optical data for a fixed frequency (lower curve) in Fig. 6. Data are shown for four samples with three different thicknesses. The samples were heated at a rate of 1 K/min.

The thermal desorption curves of Fig. 6 have distinctive features in the same temperature intervals as the optical data. The overall shift of the desorption curves toward higher temperatures is caused by the fact that the diffusion of cryo-trapped nitrogen molecules toward the sample-vacuum interface is slower than the optical changes. This is confirmed by the thickness dependence of the shifted curves; when the cryocondensate is thicker, the delay in detecting a change in the pressure in the vessel is longer.

The desorption curves in Fig. 6 are not monotonically smooth. Three local extrema, which show up especially strongly in the thicker samples, can be seen. We believe that there is good reason to relate these thermal desorption features to the optical data shown in Figs. 4 and 5 and, ultimately, to the possible sequence of structural transformations in the initially amorphous samples of solid nitrous oxide.

## 4. Discussion and conclusions

Despite some substantial differences in the experimental setups and the character of the results obtained, we believe that the data presented in this article, both our own and those of our colleagues, are a manifestation of the characteristic behavior of nitrous oxide, especially the two resonance modes of the  $N_2O$  molecule.<sup>1,2,24</sup> These two modes have different valence bonds, electronic configurations in their outer shells, and, therefore, different dipole moments. This is indicated by the data of Ref. 25, where the possibility, in principle, of isomorphic forms of the  $N_2O$  molecule (Fig. 7) was discussed.

Before explaining the data, it is necessary to make a few important assumptions:

- first, in the gaseous phase, nitrous oxide is a mixture of two equilibrium resonance modes with in a certain concentration ratio;
- second, the equilibrium concentrations of the two resonance modes of nitrous oxide differ substantially in the gaseous and solid phases;
- third, the equilibrium concentration of the two modes in the solid phase depends on the condensation temperature, but also on the current temperature of the sample; and,

fourth, relaxation processes take place in solid nitrous oxide that are related to the concentration disequilibrium of the two resonance modes; the dynamics of these processes arise from the thermodynamic prehistory of the sample during fabrication and afterward.

Given these assumptions, we can attempt to explain our data.

- 1. Cryocondensation emission of nitrous oxide.<sup>4-7</sup> The process of cryocondensing nitrous oxide on a substrate is accompanied by a sudden change in the equilibrium concentrations of the two resonance modes of N<sub>2</sub>O in the solid phase relative to the gaseous phase. At relatively high condensation temperatures (90-130 K), the mobility of the molecules is very large and relaxation takes place at a high rate. This involves a sharp change in the dipole moments of a substantial fraction of the nitrous oxide molecules, both in magnitude and in spatial orientation. One consequence is the appearance of electromagnetic radiation in the form of short, intense bursts. Lowering the condensation temperature leads to freezing of the nonequilibrium modes, which enter a stable state as the temperature of the condensate is raised. This leads to steady (constant luminosity) emission.
- 2. The shift in the absorption bands of the characteristic vibrations of the nitrous oxide molecule in the neighborhood of T = 40 K (Figs. 3 and 4). The basic explanation for this phenomenon is also based on the idea of isomorphic structures of the nitrous oxide molecule. At temperatures below and above the transformation temperature T = 40 K, nitrous oxide molecules corresponding to the cyclical and linear isomorphs can be found at the cubic lattice sites (Fig. 8).

lecular vibrations, which is observed in our experiments. The fact that the transition takes place at different temperatures for the different vibrational modes may be related to a difference in the binding energies and the associated activation energies.

<sup>a)</sup>Email: Andrei.Drobyshev@kaznu.kz

- <sup>1</sup>H. Okabe, *Photochemistry of Small Molecules* (John Wiley & Sons, 1978).
- <sup>2</sup>W. C. Trogler, Coord. Chem. Rev. **187**, 303 (1999).
- <sup>3</sup>C. E. Wayne and R. P. Wayne, *Photochemistry* (Oxford University Press, 1996).
- <sup>4</sup>A. S. Drobyshev and D. N. Garipogly, Generation of electromagnetic radiation in the optical range during gas-solid phase transitions [in Russian], Alma-Ata (1988), 8 pp. (Manuscript deposited in KazNIINTI, No. 2185 (1988)).
- <sup>5</sup>D. N. Garipogly and A. S. Drobyshev, Fiz. Nizk. Temp. **16**, 936 (1990) [Sov. J. Low Temp. Phys. **16**, 547 (1990)].
- <sup>6</sup>A. S. Drobyshev and E. A. Samyshkin, Instrum. Exp. Tech. **40**, 437 (1997).
- <sup>7</sup>A. S. Drobyshev, D. N. Garipogly, S. L. Maksimov, and E. A. Samyshkin, Fiz. Nizk. Temp. **20**, 600 (1994) [Low Temp. Phys. **20**, 475 (1994)].
- <sup>8</sup>A. S. Drobyshev, Fiz. Nizk. Temp. **22**, 165 (1996) [Low Temp. Phys. **22**, 123 (1996)].
- <sup>9</sup>N. V. Krainyukova, M. A. Strzhemechny, and A. S. Drobyshev, Fiz. Nizk. Temp. **22**, 455 (1996) [Low Temp. Phys. **22**, 354 (1996)].
- <sup>10</sup>N. V. Krainyukova, M. A. Strzhemechny, and A. S. Drobyshev, Czech. J. Phys. 46, 2243 (1996).
- <sup>11</sup>R. Balog, P. Cicman, N. C. Jones, and D. Field, Phys. Rev. Lett. **102**, 073003 (2009).
- <sup>12</sup>W. G. Lawrence and V. A. Apkarian, J. Chem. Phys. 97, 2224 (1992).
- <sup>13</sup>G. Geballos, H. Wende, K. Baberschke, and D. Arvanitis, Surf. Sci. 482–485, 15 (2001).
- <sup>14</sup>G. Herzberg, Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules (Van Nostrand Reinhold, New York, 1945).
- <sup>15</sup>J. L. Griggs, K. N. Rao, L. H. Jones, and R. M. Potter, J. Mol. Spectrosc. 25, 24 (1968).
- <sup>16</sup>J. L. Griggs, K. N. Rao, L. H. Jones, and R. M. Potter, J. Mol. Spectrosc. **18**, 212 (1965).
- <sup>17</sup>J. Pliva, J. Mol. Spectrosc. **27**, 461 (1968).
- <sup>18</sup>A. S. Drobyshev, N. V. Atapina, D. N. Garipogly, S. L. Maksimov, and E. A. Samyshkin, Fiz. Nizk. Temp. **19**, 567 (1993) [Low Temp. Phys. **19**, 404 (1993)].
- <sup>19</sup>A. Drobyshev, A. Aldiyarov, D. Zhumagaliuly, V. Kurnosov, and N. Tokmoldin, Fiz. Nizk. Temp. **33**, 627 (2007) [Low Temp. Phys. **33**, 472 (2007)].
- <sup>20</sup>A. Aldiyarov, M. Aryutkina, A. Drobyshev, M. Kaikanov, and V. Kurnosov, Fiz. Nizk. Temp. **35**, 333 (2009) [Low Temp. Phys. **35**, 251 (2009)].
- <sup>21</sup>A. Drobyshev, A. Aldiyarov, D. Zhumagaliuly, V. Kurnosov, and N. Tokmoldin, Fiz. Nizk. Temp. **33**, 472 (2007) [Low Temp. Phys. **33**, 355 (2007)].
- <sup>22</sup>J. Matthiesen, R. Scott Smith, and B. D. Kay, J. Phys. Chem. Lett. 2, 557 (2011).
- <sup>23</sup>A. Aldiyarov, A. Drobyshev, E. Korshikov, V. Kurnosov, and D. Sokolov, Fiz. Tverd. Tela 54, 1387 (2012).
- <sup>24</sup>J. E. Huheey, *Inorganic Chemistry, Principles of Structure and Reactivity* (Harper & Row, New York, 1983).
- <sup>25</sup>F. Wang and R. D. Harcourt, J. Phys. Chem. A **104**, 1304 (2000).

The transition from one mode to the other is accompanied by a change in the characteristic fundamental intramo-

Translated by D. H. McNeill