Orientational order parameter in α-N$_2$ from x-ray data

N. N. Galtsov, O. A. Klenova, and M. A. Strzhemechny

B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences,
47 Lenin Ave., Kharkov 61103, Ukraine
E-mail: galtsov@ilt.kharkov.ua

A method is suggested and validated for the deduction of orientational order parameter values η in molecular crystals consisting of diatomics directly from integrated x-ray diffraction intensities. This method is applied to pure solid nitrogen in its α phase. It is shown that to within a good accuracy the integrated intensity of a superstructure reflection is proportional to η^2. The η values determined from x-ray powder diffraction measurements agrees well with the values obtained by NQR and NMR.

PACS: **61.10.−i**, **61.66.−f**, **65.70.+y**

1. Introduction

Experimental determination of the orientational order parameter is an important issue for the physics of phase transitions in molecular crystals. In pure molecular crystals made up of linear molecules (N_2, CO_2, N_2O, etc.), the order parameter η is defined as a thermodynamic average of the spherical harmonic of second order in the suitable reference frame

$$\eta = \langle P_2(\cos\theta) \rangle , \qquad (1)$$

where P_2 is the Legendre polynomial; θ is the angle made by the molecular axis with the <111> direction of the *Pa*3 structure. Much effort has been spent to investigate into the problem of the temperature dependence of the order parameter and its role in the $\alpha-\beta$ phase transition (for an exhaustive overview see Ref. 1). In order to determine η values from experimental data, the resonance techniques of NMR and NQR are employed (for more details cf. [1,2]). If the disordering factor is not only temperature but positional randomness as well (as is the case in binary alloys), resonance methods can became inefficient. Reconstruction of η values in CO_2−Ar solid mixtures [3] was attempted directly from electron diffraction intensities. This approach possesses sufficient generality for application to the case of pure crystals, for example, nitrogen. First attempts to use the integrated intensities of super-structure reflections as a measure of orientational order and to evaluate the effect of large-amplitude librations date back to the sixties in diffraction measurements of Sándor and coworkers [4,5] on solid DCl and DBr. Later, with the coming of computer era, it became feasible to construct and probe models for the calculation of the molecular scattering factors, but the procedure is still cumbersome and the move difficult the larger are the rotational and other anharmonicities. In this connection the method suggested here does not involve any models but directly interrelate the (specifically) x-ray integrated intensities with the correctly and rigorously defined order parameter.

Although both the structure and the orientational order parameter have been thoroughly studied [6,7] over the entire domain of existence of the low-temperature α-phase of N_2, determination of η directly from diffraction data is nevertheless of interest for the following reasons. First, this is an independent method on a par with the NMR and NQR techniques [2,7]. Second, reconstruction of this kind will allow assessment of the method's efficiency and its applicability for orientational ordering of another nature and symmetry.

In Sec. 2 of this paper we present an improved modification of the method suggested previously [3] and its validation. Section 3 contains details of powder x-ray experiment. In the last section we deduce η values, compare them with the results

available from NQR measurements, and draw conclusions.

2. Theory

The integrated intensity of scattered x-ray radiation can be represented in the form [8,9]

$$I \propto \Phi(\theta) \left| \sum_s F_s(\mathbf{q}) \exp (2\pi i \mathbf{q} \mathbf{R}_s) \right|^2 , \qquad (2)$$

where summation runs over positions $\mathbf{R}_s$ occupied by nitrogen atoms in the unit cell; $\mathbf{q}$ is the momentum transfer; θ is the diffraction angle; and F_s is the scattering amplitude. Summing over pairs of nitrogen atoms within each molecule (sublattice) we obtain for the structure factor

$$F(\mathbf{q}) = 2f_N \sum_c \exp (2\pi i \mathbf{q} \mathbf{R}_c) \cos \xi(\mathbf{q} \mathbf{m}_c) . \qquad (3)$$

Here, specifically for α-N_2, f_N is the atomic scattering factor for the nitrogen atom; the summation runs over the four sublattices c of the $Pa3$ structure with $\mathbf{R}_c$ being the centers of the four molecules in the four sublattices; $\mathbf{m}_c$ is the instantaneous direction of the unit vector along the respective molecular axis in sublattice c; $\xi = 2\pi d/a$, where $d = 0{,}54895$ Å is half of the interatomic spacing in the nitrogen molecule; a is the lattice parameter, which is in principle temperature dependent. For $T = 0$ and $a = 5.648$ Å, $\xi = 0.61058$. Further we expand the cosine in Eq. (3) in spherical harmonics by making use of the known formula [10]

$$\cos [\xi(\mathbf{q} \mathbf{m}_c)] = \sum_{\text{even } l \geq 0} -\frac{l}{2}(2l + 1)j_l(\xi q)(\mathbf{C}_l(\mathbf{n}) \cdot \mathbf{C}_l(\mathbf{m}_c)) . \qquad (4)$$

Here $j_l(y)$ are the spherical Bessel functions; the summation is over even l;

$$(\mathbf{C}_l(\mathbf{n}) \cdot \mathbf{C}_l(\mathbf{m}_c)) = \sum_{m=-l}^{l} C_{lm}^*(\mathbf{n}) C_{lm}(\mathbf{m}_c) , \qquad (5)$$

where $C_{lm}(\mathbf{n})$ and $\mathbf{C}_l(\mathbf{n})$ are Racah's spherical harmonics and the respective spherical tensors [10]; $\mathbf{n}$ is the unit vector along $\mathbf{q}$, while q is the length of the momentum transfer vector. As will be shown below, the expansion in Eq. (4) when truncated at the second term coincides reasonably well (typically, to within 0.5–3%) with the exact results, i.e.

the terms with $l \geq 4$ can be treated as rather small corrections. It can be shown (see Appendix) that the $l = 2$ term after averaging yields precisely the orientational order parameter in Eq. (1):

$$\overline{C_{2m}(\mathbf{m}_c)} = \eta C_{2m}(\mathbf{m}_{c0}) , \qquad (6)$$

where $\mathbf{m}_{c0}$ are the unit vectors along the corresponding cube diagonals in the $Pa3$ structure. Finally,

$$\overline{\cos [2\pi x(\mathbf{q} \mathbf{m})_c]} \simeq j_0(\xi q) - 5\eta j_2(\xi q)(\mathbf{C}_2(\mathbf{n}) \cdot \mathbf{C}_2(\mathbf{m}_{c0})) . \qquad (7)$$

The scalar product in the right hand side can be expressed in standard angular variables:

$$(\mathbf{C}_2(\mathbf{n}) \cdot \mathbf{C}_2(\mathbf{m}_{c0})) \equiv G_c(\mathbf{q}) = \frac{3(\mathbf{n} \cdot \mathbf{m}_{c0})^2 - 1}{2} . \qquad (8)$$

Thus, the total scattering factor $F(\mathbf{q})$ can be approximated as

$$F(\mathbf{q}) \simeq 2f_N [j_0(\xi q) \sum_c \exp (2\pi i \mathbf{q} \mathbf{R}_c) -$$

$$- 5\eta j_2(\xi q) \sum_c G_c(\mathbf{q}) \exp (2\pi i \mathbf{q} \mathbf{R}_c)] , \qquad (9)$$

where $G_c(\mathbf{q})$ is defined in Eq. (8). The function $G_c(\mathbf{q})$ is just the Legendre polynomial $P_2(\cos \theta_{\mathbf{m},\mathbf{n}})$ where $\theta_{\mathbf{m},\mathbf{n}}$ is the angle between $\mathbf{q}$ and the respective axis $\mathbf{m}_{c0}$. It is well known (cf., for example, Ref. 11) that summing of $P_2(\cos \theta_{\mathbf{m},\mathbf{n}})$ over the first coordination sphere of cubic symmetry yields zero. Hence, for regular reflections, for which all factors $\exp (2\pi i \mathbf{q}_c \mathbf{R}_c)$ are unity, the second term in Eq. (9) will be absent. It can be also easily shown that for the structure under consideration the sum of the same exponential factors for superstructure reflections will yield zero in the first term in Eq. (9). Thus, the structure factor F can be represented in the form

$$F = 8f_N F_0 \qquad (10)$$

where

$$F_0^{\text{reg}} = j_0(\xi q) \qquad (11)$$

for regular reflections and

$$F_0^{\text{sup}} = -\frac{5}{4} j_2(\xi q) \sum_c G_c(\mathbf{q}) \exp (2\pi i \mathbf{q} \mathbf{R}_c) \qquad (12)$$

for superstructure reflections. The quantity ξ depends but weakly on temperature due to variations of the lattice parameter.

Let us now evaluate the error introduced when the truncation in Eq. (9) is used instead of the exact expansion in Eq. (4). To estimate the error for the simplest case $\eta = 1$ we take a few strong reflections at relatively small diffraction angles, viz., the regular reflections (111), (002), and (022) and the superstructure reflections (102) and (112). We find that the error amounts to -0.35% for (111), 1.08% for (002), and 1.52% for (002) and to 2.97% for (102) and -0.54% for (112). Thus the approximate expression is good to within an error of 3% or better, which permits use of this expression for the deduction of the orientational order parameter directly from integrated diffraction intensities. Since the integrated intensity I, Eq. (2), is proportional to the respective total structure factor squared, we conclude that the integrated intensity of a superstructure line is, to a good accuracy, proportional to η^2.

3. Experiment

There were integrated intensity ratios available [12] from x-ray studies on N$_2$ published previously [6]. However, the accuracy of those old data was insufficient for our purposes, for which reason we had to measure the powder x-ray intensities anew.

For calculations we used the data of x-ray measurements carried out in the iron radiation on a powder diffractometer DRON-3M equipped with a special-purpose helium cryostat [13]. Samples of solid nitrogen were grown by depositing the gas under study in small bursts onto a copper substrate cooled to 6–8 K. Such a condensation procedure precluded formation of a pronounced texture, which could be a serious disadvantage in obtaining reliable data on the integrated intensities. To remove internal strains, the polycrystalline samples obtained (0.1 or 0.2 mm thick with a grain size of about 10^{-4} cm) were annealed for 1 hour at $T = 28$–30 K. Except for the first pattern at 5 K, all other patterns were taken for the diffraction angles that included only the reflections (002), (102), (112), and (022). The temperature range of these studies was from 5 K to the α–β transition temperature. The temperature during a single data-taking run was stabilized to within ± 0.005 K. The errors in the determination of lattice parameters and total integrated intensities were respectively $\pm 0.02\%$ and 1%. Typical diffraction patterns are shown in Fig. 1.
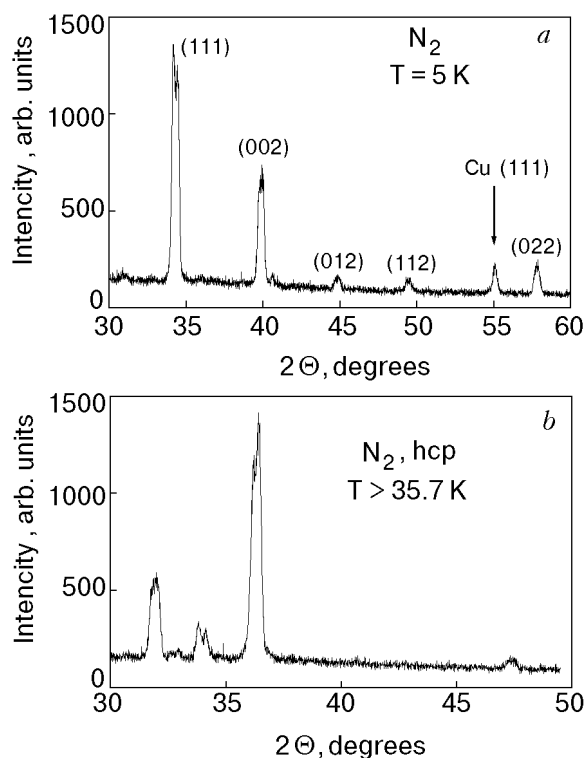

Fig. 1. Typical powder x-ray patterns for α-N$_2$ at 5 K (*a*) and slightly above the transition point, where the structure is hexagonal (*b*).

4. Results and discussion

The integrated intensities of Bragg reflections for a particular momentum transfer **q** (or the diffraction angle θ) were calculated using the formula [9]

$$I = A f_N(\theta) P(\mathbf{q}) \Phi(\theta) |F|^2 . \qquad (13)$$

Here A is a parameter, the same for all takings during a single run; $f_N(\theta)$ is the atomic scattering factor for the nitrogen atom; $P(\mathbf{q})$ is the reflection repetition number;

$$\Phi(\theta) = \frac{1 + \cos^2\theta}{\sin^2\theta \cos\theta} \qquad (14)$$

for the diffraction method used; and F is the structure factor as defined in Eq. (3). To remove the poorly defined coefficient A in Eq. (13) from further consideration, we take the ratio of the integrated intensity of a superstructure reflection (subscript s) to that of a regular one (subscript r)

$$R(\mathbf{q}_s, \mathbf{q}_r) \simeq \frac{B(\mathbf{q}_s)}{B(\mathbf{q}_r)} \left| \frac{F_0(\mathbf{q}_s)}{F_0(\mathbf{q}_r)} \right|^2 \eta^2 . \qquad (15)$$

Here F_0 are the functions defined in Eqs. (11) and (12); and $B(\mathbf{q}) = f_N(\mathbf{q})P(\mathbf{q})\Phi(\mathbf{q})$. Equation (13) allows us to obtain η values as

$$\eta \simeq \frac{F_0(\mathbf{q}_r)}{F_0(\mathbf{q}_s)} \left[R(\mathbf{q}_s, \mathbf{q}_r) \frac{B(\mathbf{q}_r)}{B(\mathbf{q}_s)} \right]^{1/2} . \quad (16)$$

We point out here that absolute η values are obtained in this way.

Our calculation procedure was as follows. From diffraction patterns for every temperature point, we determined the rms lattice parameter as well as the integrated intensities and angular positions of reflections (111), (002), (102), (112), and (022). Those data allowed us to calculate all the pertinent quantities involved in Eq. (2).

Since, as was shown above, the integrated intensities of regular reflections depend weakly on the order parameter, we can use them to assess the texture factor of our polycrystal samples. The intensity ratios between regular reflections (111), (002), and (022) give evidence that the texture was not very pronounced, amounting to about 10% with a preference for the axes of type <100>. The η values were calculated from three or four superstructure-to-regular reflection intensity ratios. An average of the η values for every temperature point are plotted in Fig. 2 as solid squares. These values compare fairly well with the η values calculated from NQR frequencies [7]. The rather large scatter of our order parameters as compared to those derived from NQR data is mainly due to the rather appreciable texture factor. We did not try to recalculate η with allowance for the texture. It is obvious that this factor will be nonexistent if diffraction data are taken on a single crystal.

In conclusion, we have shown that the orientational order parameter can be successfully calculated directly from diffraction data, either polycrystalline or single-crystal. The method applied to the orientational phase of solid nitrogen yielded results in good agreement with those obtained with resonance techniques and with the most advanced theory. Being simple and straightforward, this method allows control at every step of the calculations, and the intrinsic errors can be easily taken into account. The method can be elaborated on other types of orientational order. Moreover, this approach can be extended to other techniques (for example, optical) where the response is sensitive to the orientational order in the sample under investigation.

The authors express their gratitude to A. I. Prokhvatilov for continuous creative interest in the work and for help with the x-ray diffraction experi-
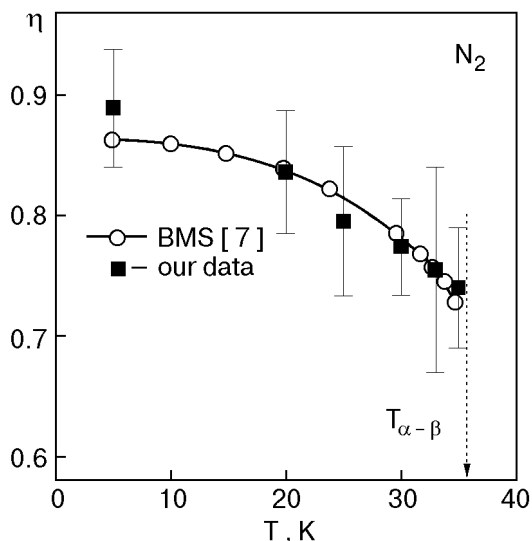

Fig. 2. Orientational order parameter as a function of temperature. The filled squares are our data; the empty circles are the data of Brookeman, McEnnan, and Scott [7]. The solid line is a guide for the eye, which virtually coincides with the self-consistent theory [14] that takes into account anharmonic and correlation effects in the rotational subsystem. The error bars for our results are mainly due to the texture of our polycrystalline samples.

ments and to Yu. A. Freiman for valuable remarks. We also thank A. I. Erenburg for communicating his old results on N_2.

This work was in part supported by CRDF (grant UP2-2445-KH-02).

Appendix

The spherical harmonics $C_{2m}(\mathbf{m}_c)$ in Eq. (7), where $\mathbf{m}_c$ are the unit vectors along the momentary orientations of the molecular axes in sublattice c, should be transformed from the laboratory frame to the same intrinsic axis, for example, <111>. Then the harmonics in the two frames will be related as

$$C_{2m}(\mathbf{m}_c) = \sum_n D_{mn}^{(2)*}(\chi) C_{2n}(\mathbf{m}_c') , \quad (A.1)$$

where $\mathbf{m}_c'$ is the vector in the old (laboratory) frame and $\mathbf{m}_c$ is the same vector in the new (intrinsic) frame; $D_{mn}^{(2)}(\chi)$ is the Wigner function, and χ is the set of angles that determine the rotation of the frame. In the absence of defects of any kind it is quite natural to assume that the molecular axes are distributed axially symmetrically [15] around the chosen z axis (direction <111>) both in time and

from site to site within the same sublattice. This means that after averaging of Eq. (A.1) only the $m = 0$ component will survive, namely (remembering that $C_{20}(\mathbf{m}_c) = P_2(\cos \theta)$),

$$\overline{C_{2n}(\mathbf{m}_c')} = \eta \delta_{n0} . \qquad (A.2)$$

Since by the definition of the angles involved $D_{m0}^{(2)*}(\chi) = C_{2m}(\mathbf{m}_{c0})$, from Eq. (A.1) we obtain within an arbitrary frame

$$\overline{C_{2m}(\mathbf{m}_c)} = \eta C_{2m}(\mathbf{m}_{c0}) . \qquad (A.3)$$

We point out once again that $\mathbf{m}_{c0}$ is the direction <111> (around which the unit vectors $\mathbf{m}_c$ fluctuate) expressed in an arbitrary (laboratory) frame.

1. *Physics of Cryocrystals*, V. G. Manzhelii, Yu. A. Freiman, M. L. Klein, and A. A. Maradudin (eds.), AIP Publishers, Woodbury (1997).
2. T. A. Scott, *Phys. Rep.* **C27**, 89 (1976).
3. M. A. Strzhemechny, A. A. Solodovnik, and S. I. Kovalenko, *Fiz. Nizk. Temp.* **24**, 889 (1998) [*Low Temp. Phys.* **24**, 669 (1998)].
4. E. Sándor and M. W. Johnson, *Nature* **223**, 730 (1969).
5. E. Sándor and R. F. C. Farrow, *Disc. Faraday Soc.* **48**, 78 (1969).
6. I. N Krupskii, A. I. Prokhvatilov, and A. I. Erenburg, *Fiz. Nizk. Temp.* **1**, 359 (1975) [*Sov. J. Low Temp. Phys.* **1**, 178 (1975)].
7. J. R. Brookeman, M. M. McEnnan, and T. A. Scott, *Phys. Rev.* **B4**, 3661 (1971).
8. M. A. Krivoglaz, *Theory of Scattering of X-rays and Thermal Neutrons by Real Crystals,* Nauka, Moscow (1967) [in Russian].
9. L. I. Mirkin, *Handbook on X-ray Analysis of Polycrystals*, GIFML, Moscow (1961) [in Russian].
10. D. A. Varshalovitch, A. N. Moskalev, and V. K. Khersonskii, *Theory of Angular Momentum*, World Scientific, Singapore (1988).
11. J. Van Kranendonk, *Solid Hydrogen*, Plenum, New York (1983).
12. A. I. Erenburg, *private communication*.
13. A. I. Prokhvatilov, I. N. Krupskii, L. D. Yantsevich, and A. S. Barylnik, *Prib. Tekhn. Experim.* **3**, 261 (1981).
14. T. N. Antsygina, V. A. Slusarev, Yu. A. Freiman, and A. I. Erenburg, *J. Low Temp. Phys.* **56**, 331 (1984).
15. J. Felsteiner and Z. Friedman, *Phys. Rev.* **B6**, 2491 (1972).