

Structure Analysis of the Disordered Cubic Phase of Rubidium Cyanide

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Abstract

With neutron diffraction the orientational distribution of the CN^- group in the disordered cubic phase of RbCN is investigated at two different temperatures. The description of the orientational distribution functions includes a coupling between rotational and translational degrees of freedom. The influence of the thermal diffuse scattering is discussed. The results are compared with the findings in KCN and NaCN.

I. Introduction

At room temperature and down to $T = 132$ K RbCN has the cubic rock salt structure ($Fm\bar{3}m-O_h^5$) with a lattice constant of 6.84 \AA (293 K). This structure implies cubic symmetry also at the sites of the CN^- ions and, consequently, orientational disorder of these dumb-bell molecules. The molecular symmetry is much lower than the site symmetry which can only be assumed on average – namely by a random distribution of the molecular orientations over several equivalent directions. Usually changes between these equivalent orientations occur on a time scale of the order of 1 ps. Below 132 K RbCN is in a monoclinic phase with orientationally ordered CN^- ions (Parry, 1962). It is suggested that the CN^- groups are aligned along the [111] direction in this ordered phase. This is in contrast to NaCN and KCN which both have an orthorhombic structure below the orientationally disordered phase and molecular orientations along [110]. In this phase there is still disorder with respect to the ‘head–tail ordering’ of the CN^- groups (Kondo, Shoemaker & Lüty, 1979) which is removed – at least in KCN and NaCN – at another phase transition at lower temperature. As regards the details of these and other high-pressure phases, papers by Dultz & Krause (1978) and Dultz, Otto, Krause & Buevoz (1981) also report a generalized phase diagram of the alkali cyanides.

The main aim of the present study is the determination of the orientational probability distribution function (p.d.f.) of the CN^- ions in the orientationally disordered phase of RbCN. In order to obtain some insight into temperature effects, data were recorded at two temperatures, namely 150 and 293 K, that is close to the orientational order–disorder phase transition and far above it. The same temperatures were used for the measurements of phonon dispersion curves in the high-temperature phase I of RbCN which allows a direct comparison (Ehrhardt, Press, Lefebvre & Haussühl, 1980; Ehrhardt 1981). We shall refer to these measurements in the last section of this paper. Structure analyses in the disordered phase of KCN and NaCN have been reported by Rowe, Rush, Vagelatos, Price, Hinks & Susman (1975). Their results will be used for comparison as well.

The main problem in analysing orientationally disordered structures such as the high-temperature phase of the alkali cyanides is the proper description of the orientational p.d.f. In the present case a concept has been used which takes an angle-independent p.d.f. as a starting point. Deviations from complete disorder, that is a modulation of the density distribution, are introduced by symmetry-allowed surface harmonics (Kurki-Suonio, 1967; Seymour & Pryor, 1970; Press & Hüller, 1973; Dolling, Powell & Sears, 1979; Press, Grimm & Hüller, 1979; Kara, 1982; Kara & Kurki-Suonio, 1981). This choice is guided by the wish to select a model adapted to the dynamical properties of the crystal with a minimum number of variable parameters. In the following we shall adopt the notation of Press, Grimm & Hüller (1979). One interesting aspect concerns the coupling between translational and rotational degrees of freedom. Obviously the coupling between the orientation of the CN^- groups and the position of the Rb^+ ions is of decisive importance for the ordering transition (Michel & Naudts, 1977). One may ask whether a rotation–translation coupling is also reflected in the structural properties. In other systems with rotating dumb-bell molecules, e.g. NaOH, KOD

(Bleif, 1978; Kara, 1982), rather similar questions arise.

II. Experimental

The crystal used in our study was a cube with dimensions $3.5 \times 3.5 \times 3.5$ mm and a mosaic spread of about 0.35° . As RbCN is very hygroscopic, the crystal was always kept and handled under argon gas. For the present measurements, in particular, the crystal was enclosed in a thin-walled aluminium container.

The measurements were done with the automatic four-circle diffractometer P110 at the FR2 reactor of the Kernforschungszentrum Karlsruhe using a vertically focusing Cu(220) crystal as monochromator. The data were collected at an incident wavelength of 0.92 \AA with the ω -scan technique. For the measurements at 150 K the He continuous-flow cooling system of P110 (Heger, Massing, Guth, Reimers & Paulus, 1981) was used. The long-time stability of the experiment was examined by measuring the intensity of two standard reflections after every 40 reflections.

At room temperature 160 reflections were measured, and at 150 K 180 reflections. These were reduced to 46 independent reflections each.* At both temperatures we were able to observe reflections up to ninth order (*i.e.* scattering vector $|\mathbf{Q}| \simeq 9.25 \text{ \AA}^{-1}$). An obvious feature of our data was the fact that the intensity of the *ggg* reflections (*i.e.* all Miller indices h, k, l even) decreases much faster with increasing momentum transfer than the intensity of *uuu* reflections (*i.e.* h, k, l all odd).

III. Description of the orientational p.d.f.

As indicated in the introduction we want to use a description of the orientational p.d.f. which includes a coupling between rotational and translational degrees of freedom (Press, Grimm & Hüller, 1979; Kara, 1982). The molecular groups are taken as rigid ions. At this point we must emphasize that in a diffraction experiment only the coupling between different degrees of freedom of a given molecule is observed. The coupling between the CN^- orientations and the motion of alkali ions, which leads to a softening of a transverse acoustic phonon mode (Haussühl, 1973) and – in a measurement without energy analysis – to enhanced diffuse scattering ('critical scattering'), does not directly affect the orientation p.d.f. The density distribution $\rho(\mathbf{r})$ of a rigid molecule can be written as follows (Press, Grimm & Hüller, 1979):

$$\rho(\mathbf{r}) = \int \rho_T(\mathbf{R}) \rho_{\text{rot}}(\mathbf{r} - \mathbf{R} | \mathbf{R}) d\mathbf{R}. \quad (1)$$

This formulation accounts for both rotational and translational degrees of freedom which need not be independent and is particularly well suited for the description of molecules with little orientational localization. For an equivalent formulation adapted to pronounced orientational localization the reader is referred to the book of Willis & Pryor (1975) and references therein.

In (1) ρ_T means the p.d.f. for the position \mathbf{R} of the molecular centre of mass and $\rho_{\text{rot}}(\mathbf{r} - \mathbf{R} | \mathbf{R})$ is the conditional probability of finding a scatterer at $\mathbf{r} - \mathbf{R}$, if the molecular centre of mass is at \mathbf{R} . The vector $\mathbf{d} = \mathbf{r} - \mathbf{R}$ connects an atom within a molecule with its centre of mass.

For translational displacements $\mathbf{u} = \mathbf{R} - \mathbf{R}_0$ (\mathbf{R}_0 equilibrium position) a Taylor expansion of $\rho_{\text{rot}}(\mathbf{d} | \mathbf{R})$ reads, up to second order,

$$\rho_{\text{rot}}(\mathbf{d} | \mathbf{R}) = \rho_{\text{rot}}^{(0)}(\mathbf{d}) + \rho_{\text{rot}}^{(1)}(\mathbf{d})\mathbf{u} + \frac{1}{2}\mathbf{u}\bar{\rho}_{\text{rot}}^{(2)}(\mathbf{d})\mathbf{u} + \dots \quad (2)$$

with

$$\rho_{\text{rot}}^{(0)}(\mathbf{d}) = \rho_{\text{rot}}(\mathbf{d} | \mathbf{R})|_{\mathbf{R}=\mathbf{R}_0} \quad (3a)$$

$$[\rho_{\text{rot}}^{(1)}(\mathbf{d})]_i = \frac{\partial}{\partial R_i} \rho_{\text{rot}}(\mathbf{d} | \mathbf{R})|_{\mathbf{R}=\mathbf{R}_0} \quad (3b)$$

$$[\rho_{\text{rot}}^{(2)}(\mathbf{d})]_{ij} = \frac{\partial}{\partial R_i} \frac{\partial}{\partial R_j} \rho_{\text{rot}}(\mathbf{d} | \mathbf{R})|_{\mathbf{R}=\mathbf{R}_0}. \quad (3c)$$

As $\rho_{\text{rot}}(\mathbf{d} | \mathbf{R})$ has the full site symmetry, all terms in the expansion given above have this symmetry, too. The first term (3a) refers to the standard expression in the absence of a rotation–translation coupling. Equations (3b) and (3c) give correction terms whose importance decreases with the order l of $\rho^{(l)}$.

By a Fourier transformation and the assumption of a Gaussian probability density function $\rho_T(\mathbf{R})$ with isotropic mean-squared amplitudes (*i.e.* a harmonic description of the translational motion which certainly represents an approximation in view of the large thermal amplitudes in the whole range of temperature) the structure factor $F(\mathbf{Q})$ reads (Press, Grimm & Hüller, 1979)

$$F(\mathbf{Q}) = \exp[-W(\mathbf{Q})] \exp(i\mathbf{Q}\mathbf{R}_0) \sum_k F_k(\mathbf{Q}). \quad (4)$$

$W(\mathbf{Q})$ is the Fourier transform of $\rho_T(\mathbf{R})$, and the $F_k(\mathbf{Q})$ describe the influence of rotations and the coupling to the translations. One finds for F_0 and F_1

$$\begin{aligned} F_0(\mathbf{Q}) &= \int \rho_{\text{rot}}^{(0)} \exp(i\mathbf{Q}\mathbf{d}) d\mathbf{d} \\ &= 4\pi \sum_{l'm'} i^l j_l(Q|\mathbf{d}|) c_{l'm'} K_{l'm'}(\Omega_{\mathbf{Q}}) \end{aligned} \quad (5a)$$

$$\begin{aligned} F_1(\mathbf{Q}) &= 4\pi \sum_{l'm'} (-i)^{l'+1} \langle u^2 \rangle c_{l'm'}^{(1)} \cdot \mathbf{Q} \\ &\quad \times j_{e'}(Q|\mathbf{d}|) K_{l'm'}(\Omega_{\mathbf{Q}}). \end{aligned} \quad (5b)$$

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38153 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The $j_\nu(Q|\mathbf{d}|)$ are spherical Bessel functions with the argument $Q|\mathbf{d}|$, (Ω_Q) denotes the polar angle of the scattering vector \mathbf{Q} , and the $K_{l'm'}$ (Ω_Q) are symmetry-adapted surface harmonics.

The contributions to $F_0(\mathbf{Q})$ are well known. Only surface harmonics which are invariant under all symmetry operations of the point group $m\bar{3}m$ need to be included: $K_{01}(\Omega)$, $K_{41}(\Omega)$, $K_{61}(\Omega)$, $K_{81}(\Omega)$, etc. Concerning the additional contributions we have to specify the dumb-bell character of the CN^- group somewhat better. Within a coordinate system rotating with the molecular ion ('molecular frame') one can define an asymmetric and a symmetric dumb-bell. In terms of the scattering-length density $b(\mathbf{r})$ we can write

$$b(\mathbf{r}) = b_{\text{sym}}(\mathbf{r}) + b_{\text{asym}}(\mathbf{r}) \quad (6)$$

$$\text{with } b_{\text{sym}}(\mathbf{r}) = \frac{1}{2}(b_{\text{N}} + b_{\text{C}}) \{ \delta(\mathbf{r} - \mathbf{d}) + \delta(\mathbf{r} + \mathbf{d}) \} \quad (7a)$$

$$\text{and } b_{\text{asym}}(\mathbf{r}) = \frac{1}{2}(b_{\text{N}} - b_{\text{C}}) \{ \delta(\mathbf{r} - \mathbf{d}) - \delta(\mathbf{r} + \mathbf{d}) \}. \quad (7b)$$

Here $\pm \mathbf{d}$ denotes the positions of the C and N atom, respectively, in the molecular frame. We neglect that the centre of mass lies off the middle of the CN^- group, since we convinced ourselves that this approximation affects the structure factor by less than 0.005 $|\mathbf{Q}|$.

Since only harmonics $K_{l'm'}$ contribute to $F_1(\mathbf{Q})$ which transform like \mathbf{Q} (that is like a vector) there is no such term for the symmetric part of the dumb-bell $b_{\text{sym}}(\mathbf{r})$ which has inversion symmetry. There is a contribution of the asymmetric part only. For $F_2(\mathbf{Q})$ the situation is reversed. For symmetry reasons there is a contribution of $b_{\text{sym}}(\mathbf{r})$ only which reads as follows:

$$F_2(\mathbf{Q}) = F_2^A(\mathbf{Q}) + F_2^{Es}(\mathbf{Q}) + F_2^{T_{2s}}(\mathbf{Q}) \quad (8)$$

with

$$F_2^A(\mathbf{Q}) = 4 \{ 3 \langle u^2 \rangle - \langle u^2 \rangle^2 Q^2 \} \times [c_{01}^{(2)A} j_0(Qd) + c_{44}^{(2)A} j_4(Qd) K_{41}(\Omega_Q) + \dots] \quad (9a)$$

$$F_2^{Es}(\mathbf{Q}) = -4/3 \pi Q^2 \langle u^2 \rangle^2 [c_{41}^{(2)E} j_2(Qd) \times \{ 3[K_{41}(\Omega_Q)] + 4/5 \} + \dots] \quad (9b)$$

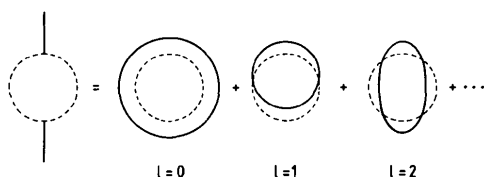


Fig. 1. Schematic representation of an expansion of the orientational p.d.f. of a dumb-bell in the symmetry-adapted surface harmonics. For cubic site symmetry only the term $l = 0$ is allowed (plus an additional term of order $l \geq 4$). The terms with $l = 1$ enters by a linear coupling ('asymmetric molecule') in the translation, the term with $l = 2$ by a quadratic coupling (symmetric molecule).

$$F_2^{T_{2s}}(\mathbf{Q}) = 4\pi Q^2 \langle u^2 \rangle^2 [c_{41}^{(2)T} j_2(Qd) \times \{ [K_{41}(\Omega_Q)] - 2/5 \} + \dots]. \quad (9c)$$

The expression for F_2^{Es} is missing in the paper by Press, Grimm & Hüller (1979).

At this point one may already suspect that the terms $F_1(\mathbf{Q})$ and $F_2(\mathbf{Q})$ represent rather weak corrections only. The scattering lengths are $b_{\text{C}} = 6.6484$ and $b_{\text{N}} = 9.36$ fm. Consequently the term weighting F_2 is rather large as $b_{\text{C}} + b_{\text{N}} = 16.0$ fm. On the other hand it is a correcting term in second order of the translational displacements, only. F_1 , which is the lowest-order contribution to $\rho_{\text{rot}}(\Omega)$, is weighted with the small difference $b_{\text{N}} - b_{\text{C}} = 2.71$ fm. It was not possible to see the influence of the F_1 contribution in the numerical calculations. A short interpretation of the physical meaning of F_0 , F_1 and F_2 is given in Fig. 1.

IV. Results and discussion

First the measured structure factors were fitted with the standard expression, *i.e.* only the term F_0 in (5a) was retained and the following parameters were introduced: a scale factor S , a parameter for correction of secondary extinction ε , a mean-squared amplitude $\langle u_{\text{Rb}}^2 \rangle$ for the Rb^+ ion and a mean-squared amplitude $\langle u_{\text{CN}}^2 \rangle$ for the CN^- ion, the length of the dumb-bell $2d$ and the coefficients $c_{41}^{(0)}$, $c_{61}^{(0)}$, $c_{81}^{(0)}$, [$c_{00}^{(0)} = 1$ by definition]. This is the same procedure as that used by Rowe *et al.* (1975) who included the expansion coefficients $c_{41}^{(0)}$ and $c_{61}^{(0)}$. The best results were achieved at 150 K with $c_{61}^{(0)}$ and $c_{81}^{(0)}$ fixed at zero and at room temperature with $c_{81}^{(0)}$ fixed at zero and without corrections for extinction [the most intense reflection (200) was excluded from the refinement at room temperature in order to minimize the number of fitting parameters; *i.e.* avoiding correction for extinction]. The parameter values are given in Table 1, a comparison with the KCN and NaCN values (Rowe *et al.*, 1975) is given in Table 2. Figs. 2 and 3 show the orientational probability distribution function in stereographic projection. The maximum of this distribution is found to be along a [111] and the minimum to be along a [100] direction. It should be remarked that KCN has the maximum probability in a [111] direction also, while NaCN has the maximum in a [100] direction (Rowe *et al.*, 1975). It is obvious that the distribution function at room temperature displays considerably more modulation than that at 150 K. The same effect has been reported for KCN and NaCN where the distribution function is also more spherical near T_c than far above it (Rowe *et al.*, 1975). This result cannot be understood within the framework of a temperature-independent single-particle potential. A fit with $c_{41}^{(0)}$ also fixed at zero — *i.e.* an isotropic distribution — yields a weighted reliability factor

Table 1. Parameters of the model refinements (dashes mean that the inclusion of this parameter did not improve the fit)

	150 K	150 K	293 K	293 K
Scale factor	28.16 ± 0.62	28.24 ± 0.58	24.03 ± 0.65	22.85
Extinction	0.039 ± 0.009	0.040 ± 0.009	—	—
$\langle u_{\text{Rb}}^2 \rangle$ (Å ²)	0.0643 ± 0.0007	0.0643 ± 0.0007	0.0633 ± 0.0008	0.0615 ± 0.0004
$\langle u_{\text{CN}}^2 \rangle$ (Å ²)	0.0590 ± 0.0013	0.0633 ± 0.0010	0.0634 ± 0.0011	0.0639 ± 0.0005
Half dumb-bell length (Å)	0.5911 ± 0.0015	0.5805 ± 0.0025	0.5854 ± 0.0015	0.5867 ± 0.0008
$c_{41}^{(0)}$	-0.151 ± 0.024	—	-0.350 ± 0.027	0.43 ± 0.11
$c_{61}^{(0)}$	—	—	0.51 ± 0.22	0.43 ± 0.11
$c_{41}^{(0)}$	—	-7.0 ± 2.8	—	—
$c_{41}^{(0)A}$ (only columns 2 and 4)	—	—	—	0.17 ± 0.03
$c_{41}^{(0)M}$ (only columns 2 and 4)	—	—	—	-2.16 ± 0.26
$c_{41}^{(0)E}$ (only columns 2 and 4)	—	-0.64 ± 0.11	—	—
$c_{41}^{(0)T}$ (only columns 2 and 4)	—	—	—	—
R_w (%)	5.0	4.6	5.4	2.8
χ^2	2.0	1.8	2.9	0.77

Table 2. CN bond length (Å) and expansion coefficients

	T	$2d$	$c_{41}^{(0)}$	$c_{61}^{(0)}$
RbCN ^a	293 K	1.172 (3)	-0.151 (24)	—
RbCN ^a	150 K	1.172 (5)	-0.350 (27)	0.51 (22)
KCN ^b	295 K	1.175 (4)	-0.132 (22)	0.23 (18)
KCN ^b	180 K	1.190 (4)	-0.018 (22)	0.22 (14)
NaCN ^b	295 K	1.189 (2)	0.192 (8)	0.31 (6)

References: (a) This work; (b) Rowe, Hinks, Price, Susman & Rush (1973).

$$R_w = \frac{\sum_l |F_{ot}^2 - F_{cl}^2| \sigma^{-2}}{\sum_l \sigma^{-2} F_{ot}^2}$$

of about 7% [instead of 5.4% with non-zero $c_{41}^{(0)}$]. F_{ot} denotes the observed, F_{cl} the calculated structure amplitude and σ the standard deviation.

In the next step the contributions F_2 were introduced as well. Practically this does not affect the R_w value in the 150 K case; for the measurement at $T = 300$ K it reduced the R_w index from 5.4% to 2.8%. But this improvement is probably insignificant, as the model is fitted to a data set which is not corrected for thermal diffuse scattering (TDS). The F_2 contribution is proportional to $\langle u^2 \rangle^2$, i.e. one needs a rather large mean-squared displacement $\langle u^2 \rangle$ in order to get a sizeable contribution. Yet a large thermal amplitude $\langle u^2 \rangle$ causes a large TDS contribution to the Bragg intensities as well. On the other hand, it is very difficult to perform a correction for TDS for the measured intensities in crystals such as RbCN. Such corrections have not been attempted in the present case. Several reasons may be given: e.g. the relation between the phonon wave vector and the frequency is not linear in the relevant temperature range and therefore a correction cannot simply be based on the elastic constants. The solution of this problem should be the topic of further investigations. Two approaches appear to be possible. One consists in a convolution of known

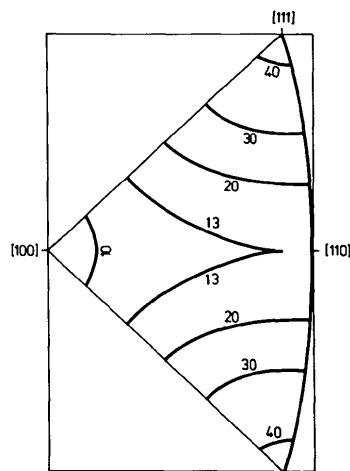


Fig. 2. Density distribution function at 293 K in stereographic projection in relative units (20 means the density of the isotropic case) using the parameter values given in column 3 of Table 1.

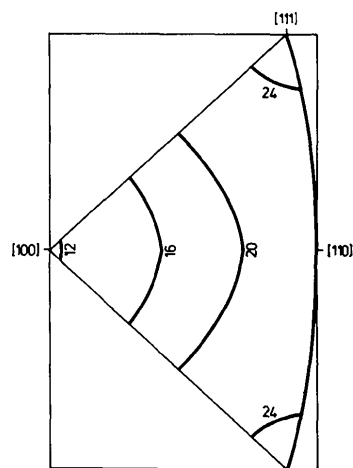


Fig. 3. Density distribution function at 150 K in stereographic projection in relative units using the parameter values given in column 1 of Table 1.

phonon dispersion with the resolution of a two-axis spectrometer. An alternative approach consists in measuring TDS-free data, as proposed, for example, by Jex, Müllner, Knoth & Loidl (1980) for KCN using Mössbauer diffraction or alternatively using a spin-echo triple-axis spectrometer with an extremely good energy resolution (Hayter, Lehmann, Mezei & Zeyen, 1979). The important influence of TDS on the measured intensities may also be concluded from the fact that the values of $\langle u^2 \rangle$ found in this paper are only about half the values derived from the lattice dynamical model mentioned above (Ehrhardt, 1981). It is well known that the intensity of high-indexed reflections is increased due to TDS and this causes values of $\langle u^2 \rangle$ which are systematically too low.

There is another remark concerning the mean-squared amplitudes: they change little between 300 and 150 K and hence considerably less than expected from the normal behaviour, namely $\langle u^2 \rangle \simeq T$. This is in agreement with investigations on KCN and with the predictions of the lattice dynamical model (Ehrhardt, 1981). The probable origin of this finding is the behaviour of the soft elastic constant c_{44} , which decreases with decreasing temperature and gives increasing mean-squared amplitudes. It should be remarked that the method used gives reliable CN bond lengths (see Table 2).

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The Chemical Bonding in Lithium Metaborate, LiBO_2 . Charge Densities and Electrostatic Properties

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Abstract

The room-temperature electron density distribution in LiBO_2 has been studied by X-ray diffraction experiments up to $s = 1.08 \text{ \AA}^{-1}$. Conventional structure refinements both with HF scattering factors for the

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neutral atoms and with the monopole parts of generalized scattering factors (GSF) calculated from the diatomic-molecule wavefunctions of LiO and BO yielded $R_w^{\text{HF}} = 0.0251$ and $R_w^{\text{GSF}} = 0.0192$ for 1266 observed reflections. The data were also used for high-order refinements with various cut-off angles in

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