

The rotational motion of NO_2^- ion in disordered phase of CsNO_2

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The orientational disorder of NO_2^- ions in the high temperature phase of CsNO_2 is examined. The potential energy at seven fundamental orientations is calculated from the first step in the molecular dynamics procedure. In order to elucidate the result of the thermal measurement by Moriya et al., the orientations which do not give the minimum energy but relate to the (111) axis in a cubic field should make a large contribution to the disorder.

I. Introduction

In ionic crystals which have the orientational disorder,¹⁾ the transition entropy $\Delta S_{\text{I-II}}$ between phases I and II might be interpreted as follows. A polyatomic ion transfers among N_{I} equivalent orientations in the surrounding field in high temperature disordered phase (phase I) whereas in low temperature phase (phase II) only a part of these equivalent orientations or N_{II} orientations has the effective contribution to the rotational motion because of the deformation of the crystal. It is supposed that the expression,

$$\Delta S_{\text{I-II}} = R \ln (N_{\text{I}}/N_{\text{II}})$$

is valid in such a case. Even if the ion has lower symmetry, the above viewpoint is suitable to its system when the ion feels the cubic field from the lattice. For instance, a nitrite ion NO_2^- forms the V-shape but its cesium salt holds the CsCl-type of crystal above 209K.

Recently, K. Moriya et al.²⁾ have made the thermal measurement of CsNO_2 , estimated the value of $\Delta S_{\text{I-II}}$, and derived that $N_{\text{I}}/N_{\text{II}}$ should be 8. They also measured the Raman spectra in which the bending mode splits into two peaks just above the transition point. And they estimated the value of N_{I} using the 2-site model according to the observed two peaks. In this paper, the static and dynamic properties of orientational disorder of NO_2^- ions in $\text{CsNO}_2(\text{I})$ is studied in terms of the molecular dynamics (MD) method.

II. The orientations of an ion

The configuration of a V-shape ion is determined by at least two vectors. However, let us express it in terms of three vectors: μ (the direction of dipole moment), τ (the direction of O-O axis) and $\nu = \mu \times \tau$ as shown in Fig. 1. The fundamental orientations of a nitrite ion in a cubic field are depicted in Fig. 2. The term fundamental orientation here refers to the orientation in which one of μ , τ , and ν vectors coincides with the (001), (011), or (111) axis in the field. But, the comprehensive orientations are not shown. In the figures, the cube corresponds to the cubic field, a big (small) circle to an oxygen (nitrogen) atom, and a dot to the center of mass of the ion. The dashed lines indicate the plane on which the ion is fixed. The hexagon on the upper right part of "e"

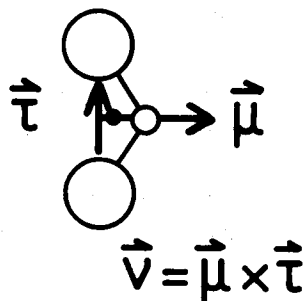


Fig. 1 Three vectors μ , τ , ν on a nitrite ion. The dipole moment corresponds to μ vector and the O-O axis is parallel to τ vector. The third vector ν is perpendicular to the plane on which the ion is fixed.

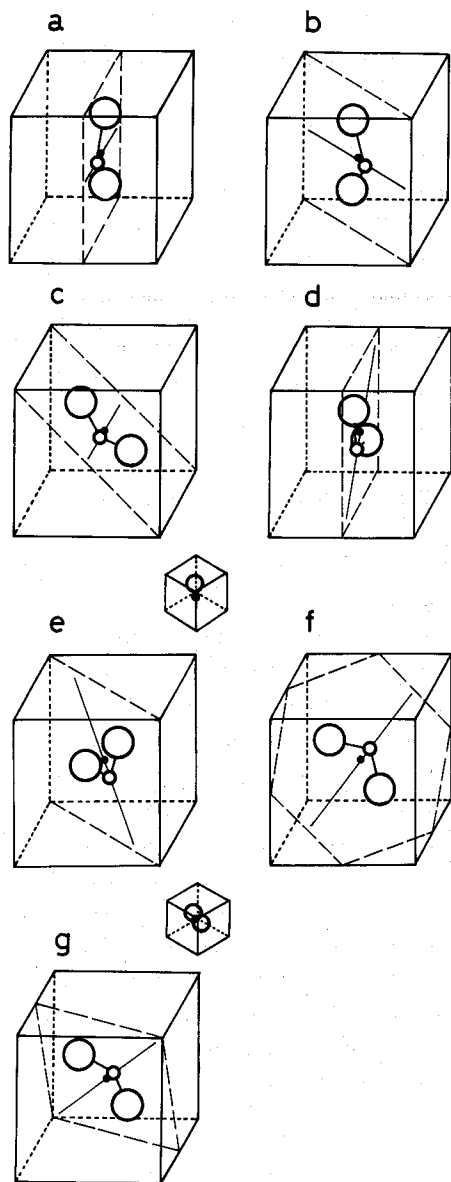


Fig. 2 Seven fundamental orientations ("a"- "g") of a nitrite ion in a cubic field. Two big circles, a small circle, a dot, and the surrounding cube represent, respectively, oxygen atoms, a nitrogen atom, the center of mass of the ion, and the field the ion senses for each orientation. The dashed lines show the plane containing the ion and the thin solid line the direction of the dipole moment. The small hexagon in "e" and "g" is the view from the (111) axis in the field.

Table 1 The fundamental orientations presented by three vectors μ , τ , ν shown in Fig. 1 or by the Euler angles $\{\alpha, \beta, \gamma\}$, and the number of equivalent orientations N.

	a	b	c	d	e	f	g
μ	100	110	100	10 $\bar{1}$	11 $\bar{2}$	211	111
τ	001	001	0 $\bar{1}$ 1	101	111	0 $\bar{1}$ 1	0 $\bar{1}$ 1
ν	0 $\bar{1}$ 0	1 $\bar{1}$ 0	0 $\bar{1}$ 1	0 $\bar{1}$ 0	1 $\bar{1}$ 0	111	2 $\bar{1}$ 1
α	0	$\pi/4$	$\pi/2$	0	0	$\lambda-\pi$	$\lambda+\pi/2$
β	0	0	$\pi/4$	$\pi/4$	λ	$\pi/4$	$\pi/4$
γ	0	0	$-\pi/2$	0	$\pi/4$	$3\pi/2$	$3\pi/2$
N	12	12	12	12	12	24	24

$$\lambda = \cos^{-1}(1/\sqrt{3})$$

and "g" is the figure seen from the (111) direction. Table 1 says the directions of the above three vectors and the Euler angles $\{\alpha, \beta, \gamma\}$, where "a" is used as a standard orientation, and the number of equivalent configurations N for each configuration "a"- "g". Attention should be called to the point that in "e", "f", and "g", one of three vectors on the ion is directed to the (111) axis in the field.

III. The static energy and the molecular dynamics calculation

The potential energy at each fundamental orientation for ferro structure is calculated from the first step of molecular dynamics (MD) run. In the MD procedure which is made as like in the case of NaNO_2 ,^{3),4)} the following potential is used. The anion has a point charge on each atom. The charge on oxygen q_o is fixed at $-0.65|e|$ and that on nitrogen q_N is determined so that the anion has the charge $-|e|$ as a whole. The Coulomb potential for long distance is summed up by Ewald method. Moreover, another type of potential:

$$U(r) = A \exp(-\alpha r) + Br^{-6}$$

acts between two atoms. For cesium, oxygen, and

Table 2 The potential parameters A, α , B in

$$U = (r) = A \exp(-\alpha r) + Br^{-6}$$

atom	A/kJ mol ⁻¹	$\alpha/\text{\AA}^{-1}$	B/kJ mol ⁻¹ \AA ⁶
Cs-Cs	5.051×10^6	3.546	-9.160×10^3
O-O	3.25×10^5	4.180	-1.085×10^3
N-N	1.76×10^5	3.780	-1.084×10^3

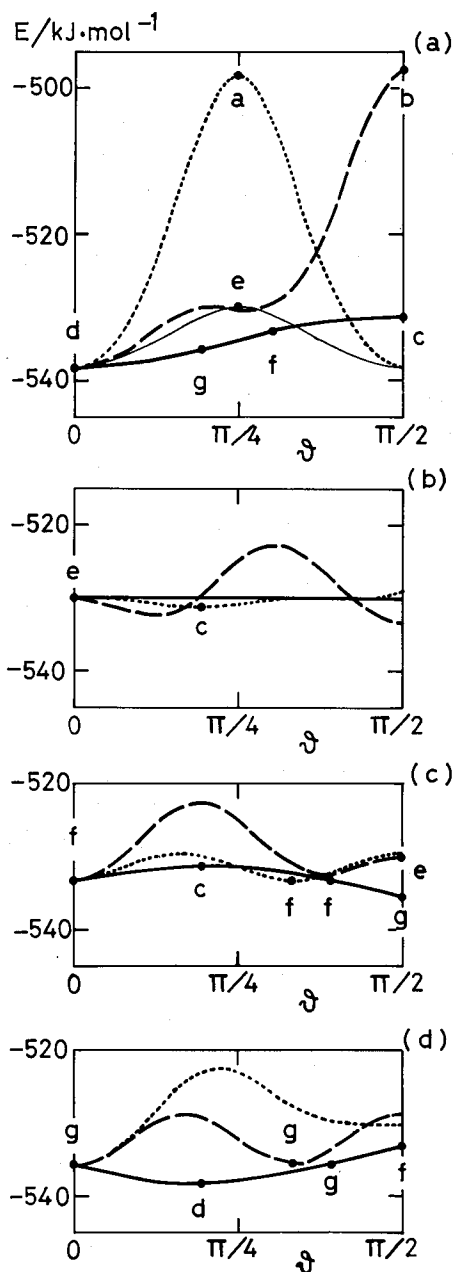


Fig. 3 The static energy in the MD run for ferro structure versus the rotational angle about τ , μ , ν vectors. The solid, dashed, and dotted curves show the variation about τ , μ , and ν vectors. In (a), (b), (c), (d), the orientation starts with "d", "e", "f", "g", respectively. In (a), the thin solid curve comes from the rotation about the (100) axis in the field.

nitrogen atoms, the potential parameters A , α , and B are shown in Table 2. The usual combination rule is adapted between different sort of atoms.

In Figs. 3 (a)–(d), the variations of the potential energy gained by the above-mentioned method are shown for the rotation about the τ , μ , and ν vectors which go through the center of mass of the ion. The solid curve represents the change about τ vector, the dashed curve about μ vector, and the dotted curve about ν vector. The initial orientation in the rotation is "d", "e", "f", "g", respectively, in Figs. 3 (a), (b), (c), (d). As seen easily from Fig. 3 (a), "a" and "b" have a quite higher energy. The rotation about the axis parallel to the O-O axis gives the sequence of "d"→"g"→"f"→"c" and the similar change is represented in Figs. 3 (c) and (d). These figures also show that "f" and "g" have the minimum energy for the rotation about μ or ν vector. Thus, "f" and "g" could be called certain saddle points.

Next, the preliminary calculation has been made by the usual MD procedure (at constant volume) just above the transition point. The primitive MD cell contains 64 ion pairs. In order to study what type of orientational disorder is realized in this phase, the orientational distribution function:

$$f(u) = \frac{1}{4\pi} \left\{ 1 + \sum_{n=2}^{\infty} c_{2n} K_{2n}(u) \right\},$$

$$c_{2n} = \langle K_{2n} \rangle \quad (u = \mu, \tau, \nu)$$

is computed for three vectors μ , τ , ν on the ion. The crystal average of the time-averaged value for each anion is denoted by the bracket $\langle \rangle$.

Table 3 The coefficients c_4 and c_6 in the orientational distribution function gained by the MD run, and their typical values.

	c_4	c_6
u	-0.50	-0.17
τ	-0.30	-0.75
ν	0.79	0.16
(001)	2.29	1.27
(011)	-0.57	-2.07
(111)	-1.53	2.27

Table 3 gives the result of c_4 and c_6 and the typical values of them. As a result, "d" mainly contributes to the orientational disorder in this case. This result reveals that the lowest energy orientation plays the significant role so that the model employed gives almost no temperature effect on the disorder.

IV. Discussions

What sort of the orientational disorder is dominant in high temperature phase depends on more or less the property of low temperature phase. Since the latter phase has the trigonal crystal structure for CsNO_2 , the former phase might be influenced strongly by the orientation for which the (111) axis in the field has the particular meaning. The orientations "f" and "g" should be correlated with the orientational disorder of this substance because ν or μ vector agrees with the 3-fold axis in the cubic field. As mentioned in Sec. III, "f" and "g" do not have the minimum energy for the rotation about τ , but the rotation about μ or ν gives the minimum energy. Therefore, "f" and "g" are non-negligible orientations because even in high temperature phase the (111) axis in the field should have a large effect. (We do not deal with "e" here because of a little higher energy.) If in the phase transition the deformation to the (111) direction occurs, the the number of

equivalent orientations for "f" reduces to 6, and for "g" also to 6. Thus, we can derive the value of N_I/N_{II} as 4 either in "f" or "g" within the scope of 1-site model. Although there is, at present, no definite theoretical ground for 2-site model, the above value becomes 8 if the model mixing of "f" and "g" is valid.

As the next step to the large MD run, we have two things to do. The first is the improvement of the point charge model of a NO_2^- ion. In the present model, near a nitrogen atom there is no big negative charge which represents the electron lone pair. The second is to find such a suitable temperature that the orientations "f" and "g" also plays the important role in the orientational disorder of $\text{CsNO}_2(\text{I})$.

The computation was made in the computer center of Institute for Molecular Science and the Nagoya University.

References

- 1) N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals* (Clarendon, Oxford, 1978).
- 2) K. Moriya, T. Matsuo, and H. Suga, *J. Phys. Chem. Solids* **44**, 1103 (1983).
- 3) M. L. Klein, I. R. McDonald, and Y. Ozaki, *Phys. Rev. Lett.* **48**, 1197 (1982).
- 4) M. L. Klein and I. R. McDonald, *Proc. R. Soc. (London) A* **382**, 471 (1982).