PHYSICAL REVIEW B VOLUME 57, NUMBER 18 1 MAY 1998-II

Neutron diffraction study of orientational freezing in $TlNO_2$ and $CsNO_2$

R. Feyerherm* and M. F. Collins
Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4M1, Canada

G. P. Johari
Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada

(Received 17 November 1997)

The low-temperature crystal structure and temperature dependence of lattice parameters and atomic mean-square displacements of thallium nitrite ($TlNO_2$) and cesium nitrite ($CsNO_2$) have been determined by neutron powder diffraction. Previously, based on specific heat and dielectric relaxation measurements, both compounds were reported to exhibit partial dynamic orientational disorder of the NO_2 anions below the transition temperatures 282.4 and 209.2 K, respectively, from the plastic, disordered high-temperature phase I to the low-temperature phase II. A glass-transition-like freezing of the associated reorientational motions was reported to occur below 60 and 40 K, respectively. In the present study, we could not confirm the previous space-group assignments $Cmmm$ and $R\overline{3}m$ for the low-temperature crystal structure of $TlNO_2$ and $CsNO_2$, respectively. Instead, we find that these compounds have space group $P3_121$ in phase II. A structural model assuming that all atoms occupy unique sites and the two oxygen atoms of each NO_2 anion are located on crystallographically equivalent sites gives excellent agreement with the observed data. This model leaves no large-angle orientational degrees of freedom for the NO_2 anion anticipated by previous studies. The glasslike behavior apparent in specific heat and dielectric relaxation studies can only be reconciled with our results if the glasslike transition involves relatively small displacements or reorientations of the NO_2 anion. This would be a novel type of glasslike transition. [S0163-1829(98)06618-1]

I. INTRODUCTION

Both $TlNO_2$ and $CsNO_2$ belong to the class of plastic crystals. Their room-temperature phase, denoted phase I, is mechanically soft and easily deformable. The phase I crystal structure has been reported previously to be of the CsCl type (space group $Pm\overline{3}m$).[1,2] The orientations of the NO_2 anions in the lattice have no long range order and the anions are likely to be freely rotating. Phase I undergoes a reversible first-order phase transition at 282.4 K for $TlNO_2$ (Refs. 3,4) and at 209.2 K for $CsNO_2$ (Ref. 4) to phase II with a lower symmetry. Previously, the lattice structure of the low-temperature phase II was reported to be of space group $Cmmm$ or (less likely) $Cmm2$ for $TlNO_2$ (Ref. 4) and $R\overline{3}m$ for $CsNO_2$.[2]

On the basis of specific heat and dielectric relaxation studies,[3,4] it was suggested that some degree of dynamic orientational disorder of the NO_2 anions persists on cooling to temperatures far below the transition to phase II. The dipolar NO_2 anions undergo increasingly slower reorientational motions in their lattice sites as phase II is cooled. These studies as well as NMR (Refs. 5,6) investigations have shown that the reorientational dynamics occurs with an Arrhenius energy of 17–19 kJ/mol for $TlNO_2$ and 14 kJ/mol for $CsNO_2$. The dipolar relaxation measurements are not sensitive to a 180° flip about the C_{2v} (twofold) axis of the NO_2 anion, because such a flip does not change the dipole moment associated with the NO_2 group. Cooling of the partially orientationally disordered crystal was thought to cause an increase in the ordered arrangement of these groups, but before a completely ordered state can be reached, the orientational dynamics slow and the reorientation time becomes comparable with the experimental time scale 5 ks for the entropy relaxation.[4,7] All configurational contributions to the thermodynamic functions appear to vanish and there is a glasslike transition at 60 K in $TlNO_2$ and 40 K in $CsNO_2$. It may be noted that this type of glasslike transition differs from that observed in monomolecular solids such as ice,[8] cyclohexanol,[9] or C_{60}.[10] In contrast to these compounds, only a part of the atoms, namely, the NO_2 anions, take part in the glasslike transition in $TlNO_2$ and $CsNO_2$, and the metal atoms do not contribute to the disorder.

The aim of the present neutron-diffraction study was to determine crystal structural information on the low-temperature phase II, including atomic sites and the possible reorientational geometry, and thus to gain insight into the microscopic details of the proposed glasslike transition. We found that for both $TlNO_2$ and $CsNO_2$ in the whole temperature range below the phase transition, phase II can be described by a highly ordered crystal structure, space group $P3_121$. Thus the previous space group assignments were not confirmed. In the present crystal structural model no degrees of freedom are left for large-scale reorientational motions of the NO_2 anion. The temperature dependence of the atomic mean-square displacements yields evidence only for small-angle orientational disorder and small-scale reorientational motions of the NO_2 anions. The glasslike behavior apparent in specific heat and dielectric relaxation studies therefore can only be reconciled with our results if the glasslike transition involves relatively small displacements or reorientations of the NO_2 anion. We believe that this would be a novel type of glasslike transition.

0163-1829/98/57(18)/11125(7)/$15.00

II. EXPERIMENTAL METHODS

$TlNO_2$ was prepared by double decomposition of 90% barium nitrite (10% barium chloride) and 99.99% thallium carbonate in an aqueous solution. Rose-orange colored microcrystals, obtained by slow evaporation of the solution at room temperature, were washed in ethanol in order to remove chloride impurities, recrystallized, and dried in a desiccator for three weeks prior to the study. A small amount of impurity in our sample is found in the neutron-diffraction patterns. A check by x-ray luminescence showed that this impurity did not contain barium. The impurity neutron powder pattern was inconsistent with the reported crystal structures of Tl_2CO_3 or TlCl and the impurity, whose concentration is estimated to less than 3%, was not identified. Nevertheless, this impurity did not interfere with our analysis of the powder patterns.

$CsNO_2$ was obtained by double decomposition of $>90\%$ barium nitrite (8% potassium perchlorate) and 99% cesium sulfate in aqueous solution. The highly soluble $CsNO_2$ was separated from the much less soluble perchlorate impurity by decanting the saturated solution. Pale-yellow microcrystals, obtained by slow evaporation of the solution at room temperature, were recrystallized and dried in an desiccator for three weeks prior to the study. No indication for the presence of chemical impurities was found in the neutron-diffraction pattern of $CsNO_2$.

The microcrystalline samples were loaded in a dry inert atmosphere into a thin vanadium tube 50 mm long and 5 mm internal diameter. This was placed in a helium-closed-cycle cryostat and the neutron powder pattern was measured on the C2 800 channel diffractometer at the NRU reactor at the Chalk River Laboratories. An incident beam of wavelength 1.3302 Å was provided by a silicon monochromator. Diffraction patterns were collected with counting times of two hours at each of the many controlled temperatures between 10 and 300 K. A more detailed description of the spectrometer and related equipment is given elsewhere.[11] Measurements made during both the cooling and heating cycle showed no measurable difference in the diffraction pattern at any given temperature. So the data taken with increasing and decreasing temperatures were combined for analysis. The accuracy of the temperature is ± 1 K. The Rietveld analysis of the neutron-powder-diffraction spectra has been carried out using GSAS.[12]

III. RESULTS

The neutron-diffraction patterns from $TlNO_2$ powder, measured at 290, 275, and 10 K are shown in the three panels in Fig. 1. The powder pattern observed at 290 K [Fig. 1(a)], in phase I of $TlNO_2$, is consistent with the CsCl type structure, space group $Pm\bar{3}m$. The lattice parameter is $a = 4.143(1)$ Å at 290 K, somewhat smaller than the value of 4.21 Å reported by Cavalca *et al.*[1] A few additional Bragg reflections in our sample appear, for example, at 19.5°, 25.6°, and 40.4°, though their intensity is too weak to be apparent in the figure. Since the intensity of these reflections varied strongly between different samples produced independently, we associate them with the small unidentified chemical impurity.

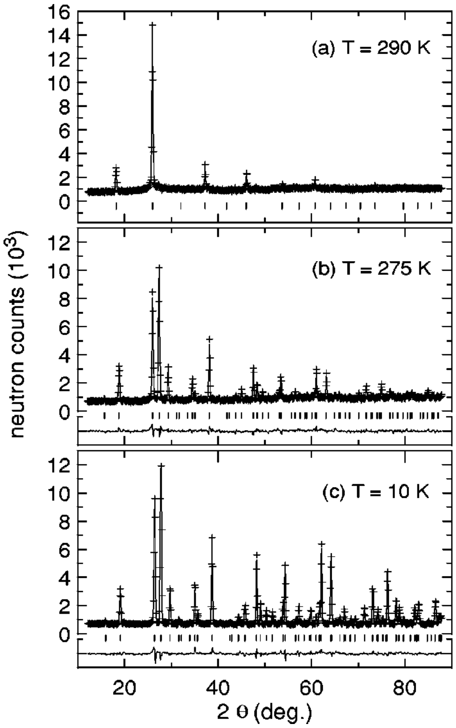

FIG. 1. The neutron powder pattern of $TlNO_2$ at (a) 290 K in its completely orientationally-disordered phase I, (b) at 275 K after the phase transition to phase II, and (c) at 10 K. The markers (+) are the data, the solid line is the Rietveld fit. The bottom of panels (b) and (c) and shows the residuals.

When the sample was cooled from 290 K, a sudden change in the diffraction pattern was observed, as shown by a comparison of Figs. 1(a) and 1(b). This corresponds to the first-order phase transition at 282 K, as noted by others using calorimetry.[3,4] Below 282 K, the overall diffraction pattern remains unchanged down to 10 K [Fig. 1(c)]. Slight changes in the positions of the Bragg reflections and a variation of their intensities indicate thermal contraction and a reduction of atomic motions on cooling. The weak Bragg reflections from the impurity did not change at the 282 K phase transition.

The observed powder pattern in the low-temperature phase of $TlNO_2$ is inconsistent with the orthorhombic symmetry, space group $Cmmm$ or $Cmm2$, suggested earlier[4] from an x-ray Laue photograph of a single crystal. Instead, we find a trigonal symmetry, namely, the enantiomorphic pair of space groups $P3_121$ and $P3_221$ matches the observed set of Bragg reflections, with lattice parameters $a = 5.6253(11)$ Å and $c = 7.4447(15)$ Å at 275 K. This corresponds to a reduction of the volume per chemical unit of $TlNO_2$ by 4.6% at the phase I → II transition. Notably, any rhombohedral space group fails to reproduce the weak but significant Bragg peak at $2\theta = 15.9°$, this is the (100) peak in the trigonal/hexagonal setting.

The two possible trigonal space groups $P3_121$ and $P3_221$ differ only in their chirality. In $P3_121$, each type of atoms forms a right-handed screw and in $P3_221$ a left-handed screw along the (001) direction with respect to the 120° rotations. From our data we cannot distinguish between these two structures, and both structural variants may occur in different crystallites. We arbitrarily chose the space group

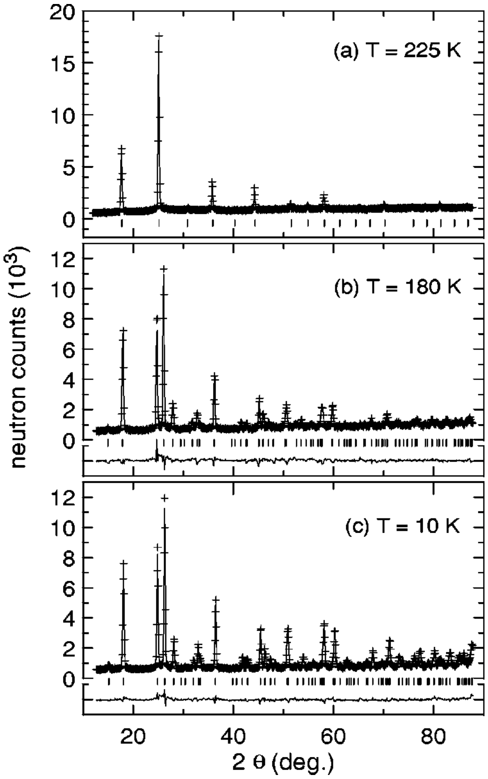

FIG. 2. The neutron powder pattern of $CsNO_2$ at (a) 225 K in its completely orientationally disordered phase I, (b) at 180 K after the phase transition to phase II, and (c) at 10 K. The markers (+) are the data, the solid line is the Rietveld fit. The bottom of panels (b) and (c) and shows the residuals.

$P3_121$ to represent the crystal structure of $TlNO_2$.

The neutron-diffraction pattern from $CsNO_2$ crystalline powder, measured at 225, 180, and 10 K is shown in the three panels in Fig. 2. The powder pattern observed at 225 K [Fig. 2(a)], i.e., in phase I of $CsNO_2$, is also consistent with the CsCl type structure, space group $Pm\overline{3}m$. The lattice parameter is $a = 4.324(3)$ Å at 225 K. At 295 K we find $a = 4.358(3)$ Å, close to the value of 4.389 Å reported previously.[2] Again, the first-order phase transition is associated with a sudden change in the diffraction pattern, as shown by a comparison of Figs. 2(a) and 2(b). Below 209 K, the overall diffraction pattern remains unchanged down to 10 K [Fig. 2(c)].

The observed powder pattern in the low-temperature phase II of $CsNO_2$ is inconsistent with the rhombohedral symmetry, space group $R\overline{3}m$, derived earlier[2] from x-ray-powder-diffraction data. Instead, we find the same trigonal space group $P3_121$ as in $TlNO_2$ by matching the observed set of Bragg reflections, with lattice parameters $a = 5.931(3)$ Å and $c = 7.853(4)$ Å at 180 K. This corresponds to a reduction of the volume per chemical unit of $CsNO_2$ by 1.4% at the phase I → II transition, much less than in $TlNO_2$.

The presence of the weak but significant (100) peak, located at $2\theta = 15.0°$, excludes a rhombohedral symmetry for $CsNO_2$, as proposed in Ref. 2. We should note, however, that in a hexagonal setting the cell parameters given in Ref. 2 are close to the ones observed in our study ($a_{\mathrm{rh}} = 4.307$ Å and $\alpha_{\mathrm{rh}} = 87.4°$ correspond to $a_{\mathrm{hex}} = 5.950$ Å and $c_{\mathrm{hex}} = 7.795$ Å).

TABLE I. Crystal structural parameters of $TlNO_2$ in space group $P3_121$.

T = 10 K			$R_p = 5.2\%$
lattice parameters	a (Å) 5.5490(5)	b (Å) 7.3233(7)	
Atom (site)	x	y	z
Tl (3a)	0.2973(9)	0.2973(9)	0
N (3b)	0.3098(8)	0.3098(8)	1/2
O (6c)	0.3715(11)	0.4940(7)	0.6182(5)
T = 275 K			$R_p = 5.7\%$
lattice parameters	a (Å) 5.6254(9)	b (Å) 7.4468(12)	
Atom (site)	x	y	z
Tl (3a)	0.2972(19)	0.2972(19)	0
N (3b)	0.3159(17)	0.3159(17)	1/2
O (6c)	0.3750(28)	0.4974(14)	0.6163(9)

In order to determine the atom positions, we carried out an initial round of Rietveld analysis on $TlNO_2$ without any constraint on the N-O distance $d_{\text{N-}O}$ or on the NO_2^- bonding angle $\beta_{\text{O-N-O}}$. The fit converged rapidly and values of $d_{\text{N-O}} = 1.25(2)$ Å and $\beta_{\text{O-N-O}} = 113.8(5)°$ were found at 10 K. At 275 K, $d_{\text{N-O}} = 1.18(4)$ Å, and $\beta_{\text{O-N-O}} = 116(1)°$. The diffraction patterns obtained for $CsNO_2$ were analyzed in the same manner, resulting in values of 1.23(2) Å and 114.8(5)° at 10 K, and 1.16(4) Å and 114(1)° at 180 K. These values are close to the values in the literature of $d_{\text{N-O}} = 1.24 - 1.26$ Å and $\beta_{\text{O-N-O}} = 113 - 115°$, observed for various nitrites.[13] The agreement of the fitted NO_2 anion geometry with the literature supports the validity of our structural model.

In the final Rietveld analysis, the N-O distance was fixed to 1.25 and 1.23 Å for $TlNO_2$ and $CsNO_2$, respectively, since it is not thought to vary with temperature. The NO_2 bond angle, however, was kept free. We fitted isotropic Debye-Waller factors to our data. Fits assuming anisotropic values for the Debye-Waller factors were unstable and thus did not yield reliable results.

The final analysis yielded the crystal structural parameters listed in Table I for $TlNO_2$ and Table II for $CsNO_2$. Notably, the change of the unit cell parameters between 10 and 275 K is very large, $\Delta a/a = 1.4\%$ and $\Delta c/c = 1.7\%$ in $TlNO_2$, resulting in a change of the unit cell volume by $\Delta V/V = 4.5\%$. The corresponding values for $CsNO_2$ are $\Delta a/a = 1.1\%$ and $\Delta c/c = 0.3\%$ and $\Delta V/V = 2.5\%$ between 10 and 180 K. The linewidths of the Bragg reflections were temperature independent and resolution limited, thus no strain effects are present. The unit cell contains three chemical units of $TlNO_2$ or $CsNO_2$ and all oxygen atoms occupy crystallographically equivalent sites. The resulting crystal structure of $TlNO_2$ is depicted in Fig. 3.

From the present lattice parameters and atom positions in $TlNO_2$ at 10 K we calculate shortest atomic distances of $d_{\text{Tl-O}} = 2.847$ Å, $d_{\text{Tl-N}} = 3.163$ Å, and a shortest nonbonding

TABLE II. Crystal structural parameters of $CsNO_2$ in space group $P3_121$.

T = 10 K			R_p=4.9%
lattice parameters	a (Å) 5.8670(7)	b (Å) 7.8304(10)	
Atom (site)	x	y	z
Cs (3a)	0.3053(13)	0.3053(13)	0
N (3b)	0.3122(8)	0.3122(8)	1/2
O (6c)	0.3755(11)	0.4768(8)	0.6147(5)
T = 180 K			R_p=5.4%
lattice parameters	a (Å) 5.9313(25)	b (Å) 7.8527(36)	
Atom (site)	x	y	z
Cs (3a)	0.3079(47)	0.3079(47)	0
N (3b)	0.3066(30)	0.3066(30)	1/2
O (6c)	0.3857(51)	0.4763(23)	0.6110(15)

N-O distance of $d_{\text{N-O}}=2.920$ Å. The shortest distance between two oxygen atoms in neighboring NO_2 anions is $d_{\text{O-O}}=3.119$ Å. In $CsNO_2$ the corresponding values are $d_{\text{Cs-O}}=3.079$ Å, $d_{\text{Cs-N}}=3.400$ Å, $d_{\text{N-O}}=3.177$ Å, and $d_{\text{O-O}}=3.298$ Å.

The values for the atom radii in the NO_2 anion are usually assumed to be close to their van-der-Waals radii $r_N=1.50$ Å and $r_O=1.40$ Å.[14] Using the values $r_{Tl}=1.40$ Å and $r_{Cs}=1.69$ Å,[15] we find that the atom packing is dense in $TlNO_2$ and $CsNO_2$. The metal to oxygen distance is close to the sum of the atom radii, hence these atoms are in contact. The metal to nitrogen distance is slightly larger than that expected from the sum of the atom radii. The nonbonding N-O distance in $TlNO_2$ is also close to the sum of the atomic radii, while in $CsNO_2$ it is significantly larger. This fact is of importance for the later discussion.

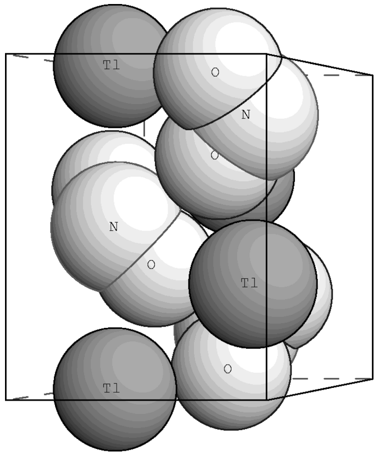

FIG. 3. Lattice structure of $TlNO_2$ in the ordered phase II. For clarity, the origin is shifted by (1/6,1/6,−1/3). The atoms are depicted with the radii $r_{Tl}=1.4$ Å, $r_N=1.5$ Å, and $r_O=1.4$ Å. The structure of $CsNO_2$ shows only minor differences in the atom positions ($r_{Cs}=1.69$ Å).

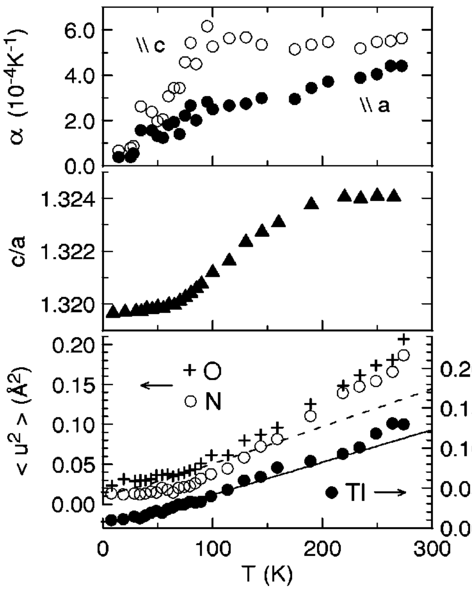

FIG. 4. Plots for $TlNO_2$ of the thermal expansion coefficient α determined from the powder patterns, the c/a ratio, and the atomic mean-square displacements $\langle u^2 \rangle$.

The temperature dependence of different parameters derived from the Rieveld refinements are summarized in Fig. 4 for $TlNO_2$ and Fig. 5 for $CsNO_2$: the temperature dependence of the thermal expansion coefficient α for the two principal lattice directions, the c/a ratio, and the mean square displacement $\langle u^2 \rangle$ (as derived from isotropic Debye-Waller factor) of the three atom types in $TlNO_2$ and $CsNO_2$.

In addition to these values, we find a smooth increase of $\beta_{\text{O-N-O}}$ in $TlNO_2$ from 113.8(5)° at 10 K to 115.4(5)° at 275 K. In $CsNO_2$, $\beta_{\text{O-N-O}}=114(1)°$ is found to be approximately temperature independent.

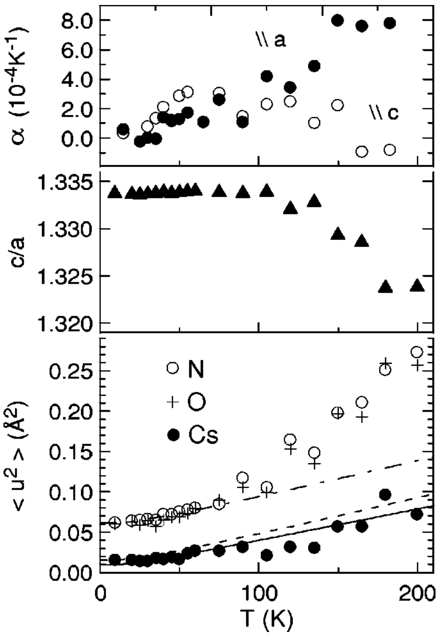

FIG. 5. Plots for $CsNO_2$ of the thermal expansion coefficient α determined from the powder patterns, the c/a ratio, and the atomic mean-square displacement $\langle u^2 \rangle$.

IV. DISCUSSION

A. Crystal structure

We first discuss the low-temperature, phase II crystal structure of $TlNO_2$ and $CsNO_2$. The space group $P3_121$ is of a much lower symmetry compared to the cubic phase I CsCl structure.

The phase I and phase II structures are related in the following way. In a first step, starting from the CsCl structure, one of the four (111) axes in the cube becomes the c axis in phase II, and the unit cell is somewhat expanded along the c axis, changing the c/a ratio from $\sqrt{3/2}=1.225$ to 1.324 for both $TlNO_2$ and $CsNO_2$, just below the phase transition temperatures. The symmetry of the resulting unit cell would be rhombohedral which was suggested earlier as the phase II structure of $CsNO_2$.[2] In a second step, the Tl and NO_2 ions are shifted toward one of the three equivalent screw axes of the rhombohedral cell, reducing the symmetry to trigonal. The N atoms are closer to the screw axis than O atoms. The positions of the two oxygen atoms of an NO_2 anion are related by symmetry with respect to a twofold axis within the trigonal plane. The described two symmetry reducing steps take place together at the first-order phase transition.

In the resulting crystal structure model, all atom sites are unique and fully occupied. There is no degree of freedom left for large-angle reorientational disorder or reorientational motions of the NO_2 ions involving different lattice sites. This is in contrast to the higher lattice symmetries proposed earlier which allowed for a set of two ($Cmmm$) or three ($R\overline{3}m$) different but crystallographically equivalent orientations of the NO_2 molecule, each of which was expected to be occupied by only one half and one third of the NO_2 groups, respectively.[2,4] A splitting of the NO_2 orientation into a pair of two crystallographically equivalent orientations would be still consistent with the present space group assignment. However, as discussed below, there is no compelling evidence for such a splitting in our data.

In order to identify a possible small-angle reorientational disorder of the NO_2 anion, we now discuss the individual isotropic atom mean-square displacements from their average position $\langle u^2\rangle$. The temperature dependences of $\langle u^2\rangle$ are shown in Fig. 4 for $TlNO_2$ and Fig. 5 for $CsNO_2$. The extrapolated values of $\langle u^2(0)\rangle$ for $T\rightarrow 0$ are listed in Table III.

In a harmonic model, the values of $\langle u^2(T)\rangle$ are related to the density of states of the vibrational spectrum $Z(\omega)$ of each unit:

$$\langle u^2(T)\rangle=\frac{3\hbar}{2m}\int Z(\omega)\frac{1}{\omega}\coth\left(\frac{\hbar\omega}{2k_BT}\right)d\omega. \tag{1}$$

Here, $\int Z(\omega)d\omega=1$, and m is the effective mass of the vibrating unit under consideration, $\hbar$ is the Plancks constant and k_B the Boltzmann factor.

In a Debye model, $Z(\omega)=3\omega^2/\omega_D^3$ (for $\omega\leqslant\omega_D$). In an Einstein model the vibrational spectrum consists of a single frequency ω_E and $Z(\omega)=\delta(\omega-\omega_E)$.

Moriya *et al.*[4] have derived values for the Debye temperature of the acoustic and the Einstein temperature of the optic vibrational modes for $TlNO_2$ and $CsNO_2$ by fitting the temperature dependence of the specific heat at low temperatures. According to the normal mode analysis, the acoustic modes describe motions of $TlNO_2/CsNO_2$ as a rigid unit, and the optic modes correspond to the relative motion of the thallium/cesium with respect to the NO_2 ions. For the latter modes, the vibrational energy is distributed between thallium/cesium and NO_2 ions in a way that the sum of their momenta is zero.

TABLE III. Observed and calculated values for the mean square displacement in $TlNO_2$ and $CsNO_2$ extrapolated for $T\rightarrow 0$.

	Observed $\langle u^2(0)\rangle$(Å^2)	Calculated $\langle u^2(0)\rangle$(Å^2)
$TlNO_2$		
Tl	0.010(2)	0.0070
N	0.013(2)	0.0135
O	0.027(4)	0.0135
$CsNO_2$		
Cs	0.015(2)	0.0084
N	0.060(3)	0.0143
O	0.060(3)	0.0143

By evaluating Eq. (1), using the values $\Theta_D=\hbar\omega_D/k_B=65.7$ K and $\Theta_E=\hbar\omega_E/k_B=189.5$ K for $TlNO_2$ and $\Theta_D=79.9$ K and $\Theta_E=176.9$ K for $CsNO_2$ from Ref. 4, we arrive at the theoretical values for $\langle u^2(0)\rangle$ listed in Table III. These values characterize the quantum-mechanical zero-point vibrations. The calculated values for the nitrogen and oxygen atoms take into account only the translational modes for the NO_2 anion as a rigid unit. They do not contain contributions from possible librational modes and internal vibrations of the NO_2 anion. The contribution from the former is certainly not negligible, but the latter are probably negligible in the temperature range under consideration.

Comparing the observed and calculated values for $\langle u^2(0)\rangle$ listed in Table III in $TlNO_2$ we find agreement for thallium and nitrogen atoms. The observed value for oxygen, however, is about a factor of 2 larger than calculated. The additional contribution to the mean-square displacement corresponds to 0.12 Å. This may either point to an additional contribution from zero-point librational motions of the NO_2 molecule or to a contribution from small static orientational disorder of the NO_2 anions. In the latter case, the mean deviation from the average orientation would be a small rotation of about $\pm 7°$, as estimated from the value of 0.12*Å and the distance of the O atoms from the NO_2 center of mass of 1.04 Å.

In $CsNO_2$ we find much larger disagreement between the observed and calculated values for $\langle u^2(0)\rangle$. The observed value for cesium is close to, but somewhat larger than calculated, and for nitrogen and oxygen the values are 4.2 times larger than calculated, pointing to a doubling of the average displacement from the equilibrium positions as compared to the zero-point motions in a harmonic model. This significant enhancement of the mean-square displacement, corresponding to 0.21 Å, again may be partly explained by additional zero-point contributions from librational modes. However, assuming the librational modes to be similar in $TlNO_2$ and $CsNO_2$, there is strong evidence for static small-angle orientational or/and small-scale positional disorder of the NO_2 anions in $CsNO_2$. The larger enhancement of the nitrogen/oxygen $\langle u^2(0)\rangle$ in $CsNO_2$ as compared to $TlNO_2$ may be related to the 0.25 Å larger value of the nonbonding N-O distance in the former (see above), leaving somewhat more space for the NO_2 molecule in $CsNO_2$.

From the overall behavior of $\langle u^2(0)\rangle$ we conclude that there is some evidence for a small-scale disorder of the NO_2 anions at least in $CsNO_2$ at low temperature. Any possible orientational disorder, however, results only from very small deviations from the average ordered crystal structure. Theoretically, this disorder could result from a splitting of the orientation of the NO_2 anion into two crystallographically equivalent orientations, each occupied randomly by half of the NO_2 anions. Such a model would still be in accord with the present space group assignment. However, the present data are consistent only with a very small spacial splitting of the nitrogen and oxygen sites. We performed Rietveld refinements of our data based on this model and did not obtain any compelling evidence for such a splitting.

B. Temperature-dependent properties

We now discuss the temperature dependence of the mean-square displacements. The theoretical temperature dependences for $TlNO_2$ and $CsNO_2$, calculated with Eq. (1), are shown in Figs. 4 and 5, respectively, as solid lines for the thallium and cesium ions and as dashed lines for the nitrogen and oxygen atoms. We find good agreement for the mean-square displacement of thallium and cesium ions in $TlNO_2$ and $CsNO_2$, respectively. This shows that these ions behave approximately as vibrating in a harmonic potential up to elevated temperatures.

The behavior observed for the NO_2 ion, however, does not correspond to the expectations from a harmonic model. In $TlNO_2$ the temperature dependences of $\langle u^2(T)\rangle$ for both the nitrogen and oxygen atoms are very similar. The two curves appear to be slightly shifted by a constant value $\Delta\langle u^2(T)\rangle = 0.015$ Å^2 (in contrast, in $CsNO_2$ the corresponding curves overlap). The observed temperature dependence of $\langle u^2(T)\rangle$ for nitrogen in $TlNO_2$ is unusual in the sense that it falls *below* the theoretical line in the temperature range 30–150 K. We are not certain whether this result is intrinsic or is related to an artifact of the least-squares fitting procedure. In the former case, the vibrational spectrum $Z(\omega)$ for the NO_2 ions would have to exhibit a lower density of states of low-energy lattice vibrations as compared with a Debye model. However, we would expect this to also show up in the $\langle u^2(T)\rangle$ data for the thallium ions, in contrast to the observations.

The temperature dependence of $\langle u^2\rangle$ for nitrogen and oxygen is linear above ≈ 75 K. For both curves the slope $d\langle u^2(T)\rangle/dT$ above 75 K is larger than expected from the harmonic model. In addition, the linear extrapolation of the observed temperature dependence for $T\rightarrow 0$, yields a *negative* intercept with the $\langle u^2\rangle$ axis. This behavior shows that above ≈ 75 K $\langle u^2(T)\rangle$ contains additional contributions not included in the harmonic model. At 275 K these account for an additional mean-square displacement of ≈ 0.03 Å^2, corresponding to a length scale of 0.17 Å.

The deviations from the harmonic behavior for nitrogen and oxygen are even more significant in $CsNO_2$. As discussed above, an enhanced value of $\langle u^2\rangle$ was already observed in the limit $T\rightarrow 0$. Even taking into account this offset (see dashed-dotted line in Fig. 5), the observed values for $\langle u^2(T)\rangle$ and the slope $d\langle u^2(T)\rangle/dT$ are larger than expected from a harmonic model above 70 K. At 200 K the additional contributions to $\langle u^2\rangle$ not included in the harmonic model account for an additional mean-square displacement of ≈ 0.17 Å^2, corresponding to a length scale of 0.41 Å. Note that this value is a significant fraction of the N-O distance of 1.233 Å.

The fact that in both $TlNO_2$ and $CsNO_2$ deviations from the harmonic model are observed for the NO_2, and not for the thallium or cesium, strongly suggests that they are related to additional motions of the NO_2 anion and not to a general anharmonicity of the acoustic lattice vibrations. Therefore, we associate this behavior with a strong anharmonicity of the librational motions of the NO_2 anions.

Our findings are difficult to reconcile with the results of several previous experiments. The excess specific heat found in a large temperature range of almost 100 K below the first-order phase transition temperatures[5] clearly shows that there is a contribution to the configurational entropy in addition to the harmonic contributions from acoustic, optic, and librational modes in this temperature range. It is unclear whether the strongly anharmonic behavior in this temperature range observed in the present experiments can fully account for this additional specific heat.

The results of dielectric relaxation measurements imply that in $TlNO_2$ and $CsNO_2$ for each NO_2 anion at least two possible orientations of its dipole moment must exist, causing a polarizability of the ensemble of NO_2 anions in the presence of an external electric field. NMR measurements confirm the presence of relaxational motions between different orientations of the NO_2 anion.[5,6] The large barrier heights ΔE between these different orientations determined in the NMR and dielectric relaxation measurements ($\Delta E/k_B = 2285$ K in $TlNO_2$ and 1680 K in $CsNO_2$) appear to be inconsistent with the possible only small-scale disorder determined in the present experiment.

At present, we cannot offer an explanation for this apparent contradiction between the present neutron-diffraction data and the previous specific heat and dipolar relaxation results. If the glasslike behavior apparent in these data involves only relatively small displacements of the NO_2 anion, as suggested by our results, both compounds $TlNO_2$ and $CsNO_2$ would exhibit a novel type of glasslike transition.

For completeness, we finally discuss the thermal expansion coefficients of $TlNO_2$ and $CsNO_2$ derived from the temperature dependence of the lattice constants are shown in Figs. 4 and 5, respectively, for both principal orientations of the trigonal lattice. In both compounds, the thermal expansion coefficient α is generally large. In $TlNO_2$, the temperature dependence of α shows a significant anomaly for expansion parallel to the c axis around 90 K. A weak anomaly around the same temperature can be noted also for the a axis. This anomaly is also reflected in the temperature dependence of the c/a ratio, depicted in Fig. 4 which is constant below 60 K but starts to increase above 60 K and reaches its steepest slope at around 90 K. Notably, the c/a ratio starts to change at the glasslike transition temperature observed in the previous specific heat and dielectric relaxation measurements.[4] This behavior strongly suggests that the anomaly in the thermal expansion is related to this transition and to the onset of additional motions of the NO_2 ion in the corresponding temperature range.

In $CsNO_2$, the data for the temperature dependence of α unfortunately are of lower quality. The temperature dependence of c/a in $CsNO_2$ does not exhibit the pronounced features as in $TlNO_2$. A slight increase of c/a, starting around 40 K, is followed by a turnover to a strong decrease of c/a above 100 K. The latter may be related to the large deviation of $\langle u^2 \rangle$ from the harmonic behavior for the NO_2 ion. In $CsNO_2$ the glass-transition-like features in the specific heat and dielectric relaxation have been observed at 40 K.

V. CONCLUSION

Our results rule out large-angle orientational degrees of freedom in phase II of $TlNO_2$ and $CsNO_2$. We do observe, however, an anomalous temperature dependence of the mean square displacement of the nitrogen and oxygen atoms. The glasslike behavior apparent in specific heat and dielectric relaxation studies can only be reconciled with our results if the glasslike transition involves relatively small reorientations of the NO_2 anion. This would be a novel type of glass transition. Single crystal studies on the low-temperature crystal structure are desirable to verify our proposed model.[16]

ACKNOWLEDGMENTS

We would like to thank R.L. Donaberger, I.P. Swainson, and D.C. Tennant for help in this experiment. The use of Chalk River Laboratories (CRL) facilities and a research grant from NSERC are gratefully acknowledged. One of us (M.F.C.) wishes to thank CRL for the hospitality during a sabbatical stay. One of us (R.F.) was supported by the Deutsche Forschungsgemeinschaft.

---

*Present address: Hahn-Meitner Institut GmbH, Abt. NE, 14109 Berlin, Germany.

[1] L. Cavalca, M. Nardelli, and I. Bassi, Gazz. Chim. Ital. **85**, 153 (1955).

[2] P. W. Richter and W. F. T. Pistorius, J. Solid State Chem. **5**, 276 (1972).

[3] K. Moriya, T. Matsuo, and H. Suga, Chem. Lett. 1427 (1977).

[4] K. Moriya, T. Matsuo, and H. Suga, J. Phys. Chem. Solids **44**, 1103 (1983).

[5] Y. Furukawa and H. Kiriyama, Chem. Phys. Lett. **93**, 617 (1982).

[6] H. Honda, S. Ishimaru, N. Onoda-Yamumoro, and R. Ikeda, Z. Naturforsch. Teil A **50**, 871 (1995).

[7] H. Suga and S. Seki, Faraday Discuss. Chem. Soc. **69**, 221 (1980).

[8] O. Haida, T. Matsuo, H. Suga, and S. Seki, J. Chem. Thermodyn. **6**, 815 (1974).

[9] K. K. Kelly, J. Am. Chem. Soc. **51**, 1400 (1929); K. Adachi, S. Suga, and S. Seki, Bull. Chem. Soc. Jpn. **41**, 1073 (1968); G. P. Johari, Ann. (N.Y.) Acad. Sci. **279**, 117 (1976).

[10] R. C. Yu, N. Tea, M. B. Salamon, D. Lorents, and R. Malhotra, Phys. Rev. Lett. **68**, 2050 (1991); G. B. Alers, B. Golding, A. R. Kortran, R. C. Hadden, and F. A. Theil, Science **257**, 511 (1992); T. Matsuo, H. Suga, W. I. F. Davis, R. M. Ibberson, P. Bernier, A. Zahab, C. Fabre, A. Rassat, and A. Dworkin, Solid State Commun. **83**, 711 (1992); G. P. Johari, J. Chem. Phys. **100**, 2220 (1994).

[11] E. Kartini, M. F. Collins, B. Collier, F. Mezei, and E. C. Svensson, Can. J. Phys. **73**, 748 (1995).

[12] A. C. Larson and R. B. van Dreele, Los Alamos Nat. Lab. Report No. LA-UCR-86-748, 1986 (unpublished).

[13] S. Ohba and Y. Saito, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **37**, 1911 (1981); M. Okuda, S. Ohba, and Y. Saito, Acta Crystallogr., Sect. B: Struct. Sci. **46**, 343 (1990); W. Bensch and A. Reller, Z. Kristallogr. **175**, 111 (1986).

[14] G. B. Carpenter, Acta Crystallogr. **5**, 132 (1952).

[15] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1960).

[16] We succeeded in growing phase II $TlNO_2$ crystals of considerable size by slow evaporation from aqueous solution held at 5 °C.