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RAMAN SCATTERING IN THE FERROELECTRIC DIGLYCINE NITRATE

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The Raman scattering in para- and ferroelectric phases of diglycine nitrate show no features connected with the transition. The critical mode is probably a very low frequency external mode associated with the motion of massive glycine groups carrying dipoles.

Key words: Raman Scattering; Diglycine Nitrate; Phase Transition; Critical Mode.

INTRODUCTION

Diglycine nitrate $(NH_2CH_2COOH)_2 \cdot HNO_3$ (DGN) undergoes a paraelectric-ferroelectric phase transition at 206 K from a centrosymmetric $P2_1/a$ space group to the polar Pa with two formula units per unit cell ($Z = 2$).[1,2] The transition appears to be of second order. It is interesting to note whereas there is a large peak of static dielectric constant at T_c comparable to that of the TGS, the value of spontaneous polarization is much smaller as compared to TGS. Sato[2] determined the structure by means of X-ray and neutron scattering and made an initial proposal as far as the mechanism of transition is concerned. Particularly, he found that the glycine zwitter-ion and the monoprotonated glycinium ion are connected by the short O—H——O hydrogen bond and that the proton is not located at the center of the H-bond but closer to the oxygen of the glycinium ion. Also, we know[3] that the transition temperature is not influenced by the deuteration. Recently, Seliger *et al.*,[4] by employing O^{17} and N^{14} NMR methods, gave the definite proof that the bond is symmetric above T_c and thus it cannot play the role as suggested by S. Sato. The infrared studies revealed no soft mode[5,6] and that the contribution of NO_3 groups to the spontaneous polarization is negligible. The atomic configurations in the glycine ions are largely similar in either phase. Nevertheless, the rotations of glycine groups are thought to be responsible for the transition. Thus a better model for the transition is needed. Seliger *et al.*[4] proposed a model where the basic reorientable dipoles are the "heavy" NH_3 and NO_3 groups to which the proton motion is coupled. They could not determine the value of critical frequency by NMR methods except that it should have been somewhat above NMR probe frequencies and thus rather low (compared to the usual optic modes). Such a low frequency has been found by Kolodziej *et al.*[7] at around few GHz by measuring the dielectric constant from

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80 MHz to 9450 MHZ. The dielectric relaxation of the Debye type with a single relaxation was observed in either phase.

To contribute to the understanding of the mechanism for the phase transition we performed the factor group analysis of the $k = 0$ phonons as well as the Raman scattering study of the phase transitions. Since the modes are either Raman or infrared active, our measurements complement the results of Khanna *et al.* and Sato.[5,6]

FACTOR GROUP ANALYSIS

The analysis is shown in the Table I. The method used here has been elucidated by Adams *et al.*[8–10] Basically, upon selecting the space group we must fill the unit cell by placing the atoms into various Wyckoff sites as defined by the International Tables for X-ray Crystallography. Each site uniquely contributes to the irreducible representations of $k = 0$ phonons.

Note that the polarization vector lying anywhere in the plane of symmetry transforms according to B_u representation. Further, we can visualize the structure above T_c as being divided into large units: glycines and nitrates. Thus the phonons can be divided into the internal and external type.[9] The latter ones can be further subdivided into translational and rotational species. Only the condensation of lattice phonons can lead to the phase transition. In the case of DGN, all atoms but N(3) belong to the general position (Wyckoff notation 4e, site symmetry 1). The two N(3) atoms are placed into 2a site (site symmetry $\bar{1}$) in paraelectric

TABLE I

Factor group analysis of DGN in the paralectric phase

Wickoff sites	A_g	B_g	A_u	B_u	Raman active	IR Active
2a–2d trans.	0	0	3	3		
4e trans.	3	3	3	3		
2a–2e rotatory	3	3	0	0		
4e rotatory	3	3	3	3		
All modes						
N(3) at 2a	0	0	3	3		
the rest at $12 \times 4e$	36	36	36	36		
N total	36	36	39	39	72	78
Translation of groups	0	0	3	3		
nitrate at 2a	3	3	3	3		
glycines at 4e	3	3	6	6		
T all	0	0	1	2		
T acoustic	3	3	5	4	6	9
T external						
Rotation of groups	3	3	0	0		
nitrate at 2a	3	3	3	3		
glycines at 4e	6	6	3	3	12	6
R external	1	2	0	0		
R crystal						
Summary	27	27	30	30	54	60
N internal	9	9	8	7	18	15
N external						

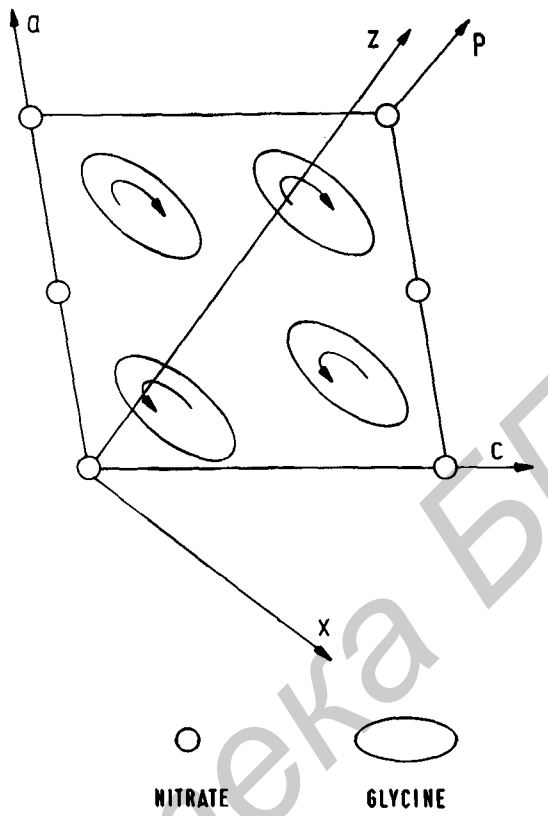

FIGURE 1 Projection of schematic structure of DGN along [010] axis. Low frequency B_u external rotational mode is shown involving the glycines. The scattering axes x and z were selected along the principal axes of indicatrix.[11] For full structure see Reference 2.

phase. The relevant part from Tables[10] is reproduced here. The distribution of all modes among irreducible representations and their activities is shown in the row labeled N total. As discussed above we can fill the structure with nitrates at site 2a as well as glycines at site 4e, Figure 1. This assignment determines the number of translational and rotational external modes and their distributions are again shown in Table I. In order to count only the optic modes the three acoustic modes must be subtracted from the list of translational external modes. We also show the representations for the solid rotation of the whole crystal. The rotational modes which transform in the same way as the solid rotations should be of the very low frequency. These latter modes are of gerade variety, not polar, however.

EXPERIMENTAL RESULTS

The crystals were attached to the cold finger of Oxford instruments CF-100 cryostat fitted with the temperature controller. We employed 180° (backscattering) optics. The frequency resolution was set at 4 cm^{-1}. The crystal was cut along

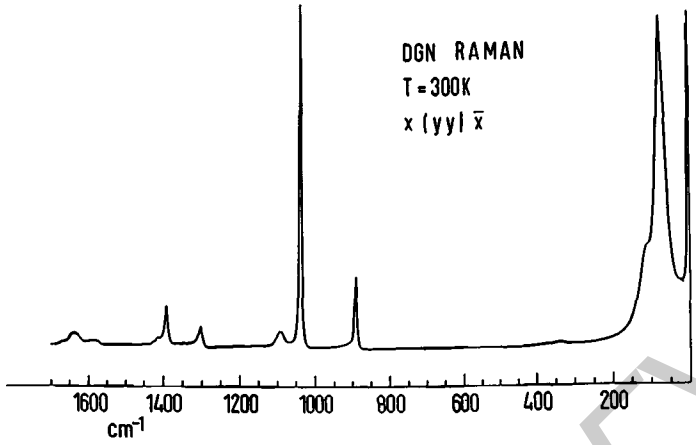

FIGURE 2 Low frequency RT x-axis scattering Raman spectrum of DGN. Symmetry is A_g.

the minor axis of optical indicatrix (z in Figure 1) which slightly deviates from the spontaneous polarization.[11]

The Raman spectra of various scattering geometries are shown in Figures 2–5. Since we had no intention to discuss chemical aspects of DGN,[5,6] only the lower frequencies are shown. X axis scattering spectra (Figures 2–3) are of much lower intensity than the Z axis ones (Figures 4–5), thus they are shown for completeness reasons only and at room temperature. Raman tensors xx, yy, zz, xz belong to the A_g representation, while yx and yz belong to the B_g. The temperature dependent spectra in both phases and for xx and xy scattering geometries are shown in Figures 4–5.

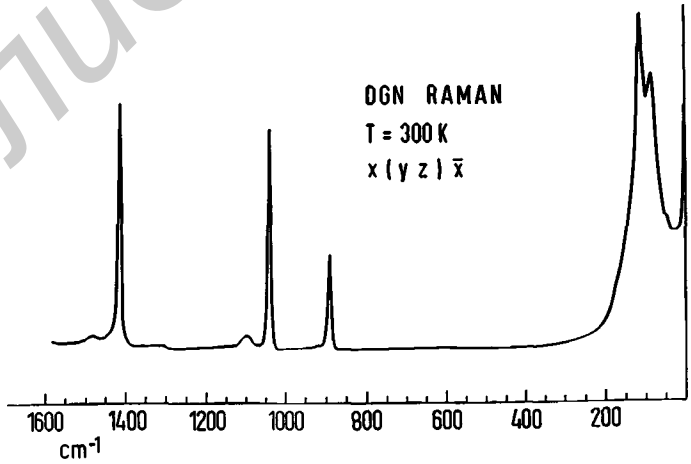

FIGURE 3 Low frequency RT x-axis scattering Raman spectrum of DGN. Symmetry is B_g.

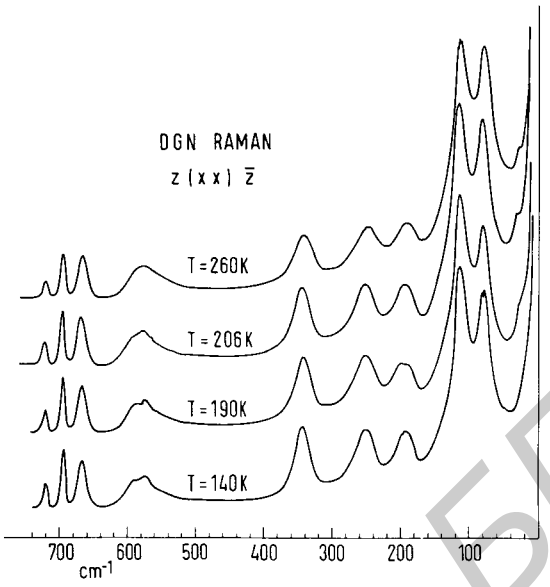

FIGURE 4 Low frequency z-axis scattering Raman spectra of DGN above and below T_c. Symmetry is A_g.

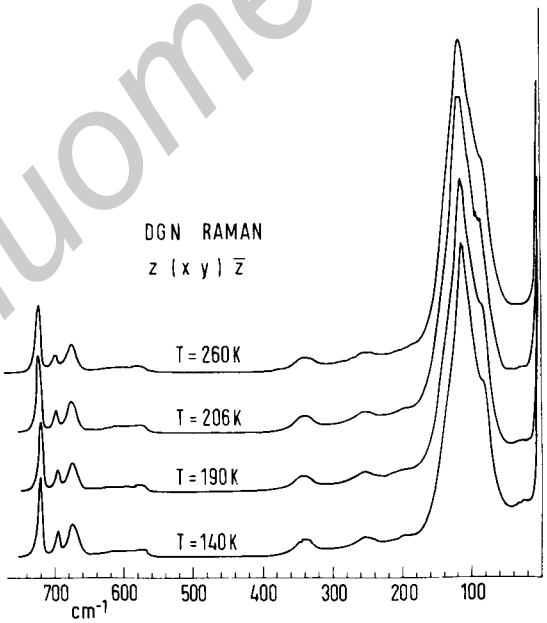

FIGURE 5 Low frequency z-axis scattering Raman spectra of DGN above and below T_c. Symmetry is B_g.

DISCUSSION

We shall concentrate on the external modes, that is on the Raman spectrum below 600 cm^{-1}. Sato[2] proposed the disordered structure above T_c with two nonequivalent glycines, almost superimposed by the inversion symmetry. Such view requires that the two glycines belong to the inversion site 2a of group. Please note that such assignment means that the site position is far away from center of gravity for glycines. In the view of Seliger *et al.*[4] results that there is only one chemical environment for the NH_3-glycines groups above and below T_c it is better and more natural to assume that all glycines are equivalent and located at the general site 4e. Furthermore, the location of glycines at 2a would result in polarity of modes only through the translations of glycines (see Table I), which would have been detected by X-ray scattering.

According to the Table I there should be $9A_g$ and $9B_g$ external modes. We have observed no such numbers, especially in the xy geometry. This is not entirely unexpected in the light of rather massive glycine groups only loosely connected. The lower frequency which could be detected was roughly 20 cm^{-1}. The A_g (xx) temperatures dependent scattering results (Figure 4) show no soft mode in the polar phase. In fact there is practically no temperature dependent mode shifts or appearances of new lines below T_c. We expected to see the "hard modes" of former ungerade symmetries arising in the polar phase with the intensities proportional to the value of spontaneous polarization.[12,13] This surprising result is somewhat consistent with the X-ray position determination.[2] In the view of dielectric measurements[7] we can safely assume that the "critical" frequency is of the order of 1–3 GHz. Recently, Rodin *et al.*[14] deduced from their Brillouin scattering results that this estimates holds.

Thus, the previous as well as the present results point to the model where we would have rather massive groups slowly rotating around two fold axis. The fact that we have a large peak in the static dielectric as well as small spontaneous polarization points to the situation where large dipoles slowly rotate thus providing resulting polarization along [101] direction. In the next step we should decide whether the rotations are nonpolar or polar. The former case appears to be attractive at the first glance since the modes have the symmetry of the rotation of the whole crystal, (see Table I, of probably very small frequency) but it should be discarded as it would require the quadratic coupling to the polarization and a condensation of mode prior to the onset of spontaneous polarization. No such case has been observed. Let us then consider the polar rotations. According to Tables I there are III such rotations of symmetry B_u involving only glycine groups.

Figure 1 shows the situation where we depict the proposed mode responsible for the transitions. The two glycines are almost perpendicular to the polarization axis. Thus the slow rotations of the glycine dipole moments under the B_u symmetry generates the polarization along [101] direction with a small spontaneous value, but with a large peak in dielectric constant. Alternatively,[15] the proposed soft mode could also be identified as the anharmonic reorientation by the finite angle-hindered rotation with the same eignevector as the above libration mode. The Raman measurements alone cannot distingusish between the two approaches.

In conclusion we measured the Raman spectra of DGN and proposed the model for the transition involving rotations of dipoles associated with the glycine groups around the twofold axis.

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