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Investigation of phase transitions in guanidinium nitrate crystals

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Abstract. Calorimetry, high-pressure dilatometry, x-ray powder diffraction and electric conduction studies were applied to investigate the phase transitions and physical properties of guanidinium nitrate, $[\text{C}(\text{NH}_2)_3]^+\text{NO}_3^-$. Two thermal anomalies related to the first-order and second-order phase transitions were observed at $T_{12} = 296$ K and $T_{23} = 384$ K, respectively. The transformation at T_{23} indicates the existence of a new high-temperature phase of guanidinium nitrate, which has been confirmed by the x-ray powder diffraction study. The transition entropies were found to be $\Delta S_{12} = 5.7$ J mol⁻¹ K and $\Delta S_{23} = 1.5$ J mol⁻¹ K. The magnitude of the change in the entropy at the 296 K phase transition indicates its order–disorder character. The change in the specific volume at T_{12} is negative, i.e. $\Delta V_{12} = -1.6$ cm³ mol⁻¹, and T_{12} linearly decreases with increasing pressure, with $dT_{12}/dp = -24.3$ K kbar⁻¹. The deuteration has only a slight effect on the temperatures of the observed phase transitions. Above 320 K an increase in electric conductivity has been noted in the polycrystalline samples of the compound studied. The results of the studies performed suggest that the mechanism of the phase transition at 296 K, accompanied by unusual deformation of the crystals, may be of an electrostatic nature.

1. Introduction

Simple guanidinium salts form a large group of crystals in which different forms of molecular disorder have been observed. Intense NMR investigations [1–8] have proved that molecular dynamics in these crystals involve mainly reorientation of $[\text{C}(\text{NH}_2)_3]^+$ cations as a whole about their threefold or pseudo-threefold symmetry axes. A few workers [2, 3, 8] have also suggested additional movement of amino groups relative to the C–N bonds. Moreover, the phenomenon of cationic self-diffusion has been observed in guanidinium perchlorate crystals and the onset of this phenomenon is associated with a structural phase transition [9].

Molecular motion involving C_3 reorientation of guanidinium cations has also been observed in crystals of guanidinium nitrate (GN), $[\text{C}(\text{NH}_2)_3]^+\text{NO}_3^-$, which are the subject of this work. GN is a molecular ionic crystal which has been found to be interesting not only in the aspect of molecular dynamics. According to recent reports, this material reveals a phase transition of first order in the vicinity of room temperature [10]. The transition from the low-temperature phase GN1 to the high-temperature phase GN2 takes place at about 296 K and shows a 20 K temperature hysteresis. Particularly impressive are the anomalous changes in the shape of the crystal accompanying this transition involving a jumpwise elongation of the crystal needle by about 45% (!) and a simultaneous reduction in its transverse dimensions [10]. This transition is also accompanied by changes in the electric

permittivity of the crystal. Unfortunately, the structure of the GN crystal is not fully known yet. However, structural investigation of other simple guanidinium salts have shown that the atoms of the $[\text{C}(\text{NH}_2)_3]^+$ ion are arranged in a plane and only hydrogen atoms can possibly take an out-of-plane position. The planar conformation of the guanidinium ion has been confirmed by the analysis of IR spectra [15]. As the NO_3^- anion has also been proved to have a planar structure, there is the possibility of formation of two-dimensional systems linked through a network of hydrogen bonds in the GN structure, which has been suggested by the preliminary results of x-ray structural investigation [16].

This paper is a continuation of our earlier work on the physical properties of GN crystals. In particular we studied the influence of a high hydrostatic pressure and deuteration on the GN1–GN2 phase transition. Extension of the temperature range of calorimetric measurements up to the melting point has led us to find a new thermal anomaly at about 384 K. The occurrence of a new high-temperature phase of GN (denoted GN3) has been supported by an x-ray powder diffraction study. The calorimetric studies and dilatometric measurements at ambient and high hydrostatic pressures provided new information on the thermodynamics of phase transitions observed in GN crystals.

2. Experimental details

The GN crystals were obtained by the method described previously [10]. The deuterated compound (denoted DGN) was obtained by repeated (a few times) crystallization of GN, as an initial substrate, from a solution in D_2O .

Calorimetric measurements were carried out by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC-7 calorimeter. Comparative studies of GN and DGN crystals were performed by the method of differential thermal analysis (DTA) using the equipment essentially described in [17].

The temperature dependence of the specific volume of a GN crystal at ambient pressure has been measured by the method of volume dilatometry in the temperature range from 250 to 505 K on a Netzsch 402 TMA dilatometer. The polycrystalline sample to be studied, obtained from the melted crystals and shaped into a cylinder 6 mm in diameter and 7.4 mm high, was immersed in silicone oil and placed in a dilatometric chamber. The temperature was changed at a rate of 2 K min^{-1} .

The effect of hydrostatic pressure on the GN1–GN2 phase transition was studied by the method of high-pressure volume dilatometry using the home-made equipment described in [18] which permitted measurements at pressures up to 1 kbar. The sample was prepared in the same way as that to be studied at atmospheric pressure, and the pressure-transmitting medium was silicone oil. The rate of temperature changes was the same as during the measurements at ambient pressure.

Electric conductivity measurements were carried out on an automatic E 315A bridge (Meratronik, Poland) at a frequency of 1 kHz in a vacuum chamber ensuring a pressure of 1 Pa. The sample was prepared by pressing the powdered crystal between metal plates of a plane capacitor.

X-ray investigation was performed on a powder diffractometer using $\text{Cu K}\alpha$ radiation. The temperature of the powdered sample was stabilized by blowing in heated air whose temperature was controlled with a PID controller.

3. Results and discussion

3.1. Calorimetric measurements

A typical temperature dependence of the specific heat of a GN crystal is shown in figure 1. The first thermal anomaly with the onset at about 298 K is related to the GN1–GN2 phase transition reported earlier [10]. The character of the anomaly as well as the observed 20 K temperature hysteresis prove that this transition is of the first order, which confirms the data obtained from DTA studies [10]. Detailed investigation by the DSC method in the vicinity of this transition for samples of different masses and different rates of temperature change reveal that the phase transition temperature determined by the onset of the anomaly may vary within a few kelvins in individual cycles which is fully consistent with earlier observations.

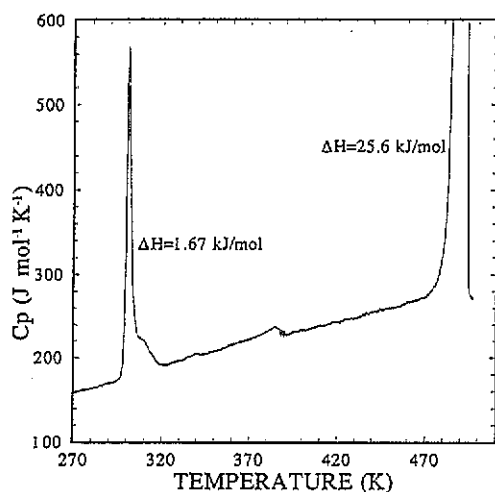


Figure 1. Molar specific heat of the GN crystal as a function of temperature.

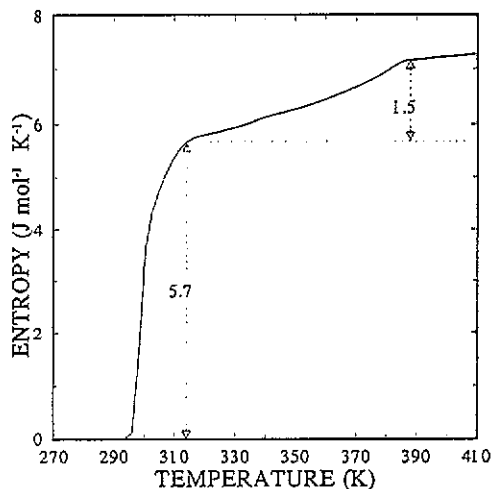


Figure 2. Transition entropies of the GN crystal.

A new feature in the temperature dependence of the specific heat of a GN crystal is another small thermal anomaly shown in figure 1 to occur between the temperature of the GN1–GN2 phase transition and the melting point $T_m = 487$ K. A characteristic of this anomaly is the long tail below the transition point stretching for about 70 K and an abrupt change in C_p at 384 K (figure 1). The shape of the $C_p(T)$ dependence as well as the lack of temperature hysteresis of this anomaly indicate that it may be related to a phase transition of second order. It should be emphasized that, in order to eliminate the possible influence of water physically adsorbed on the surface of the crystal on $C_p(T)$ [10], the DSC measurements were performed with both a closed and an opened measuring vessel, and the same results were obtained in the two cases. The anomaly at 384 K was also observed by DTA in vacuum. The observed changes in specific heat indicate the existence of the third high-temperature phase of the GN crystal above 384 K.

The molar enthalpy $\Delta H_{12} = 1.67 \pm 0.08$ kJ mol⁻¹ of the GN1–GN2 phase transition determined from DSC measurements is slightly higher than its value found by applying the DTA method [10]. In general, this value essentially depends on the choice of the baseline. As follows from the course of $C_p(T)$ dependence (figure 1), the tail of the GN1–GN2 transition from the high-temperature side overlaps the tail of the GN2–GN3 transition which makes it difficult to determine ΔH exactly.

To be able to establish the character of the observed phase transitions, we calculated the anomalous part of the molar entropy associated with these transitions. The baseline describing the specific heat not related to the phase transitions was established by approximating the $C_p(T)$ dependence from beyond the phase transition region to the region within which they were observed. The anomalous part of the molar entropy as a function of temperature was found from the following relation:

$$\Delta S(T) = \int \frac{C_p(T) - C_p^b(T)}{T} dT \quad (1)$$

where $C_p^b(T)$ stands for the baseline. The result of the integration is shown in figure 2. As follows from this figure, the GN1–GN2 transition is accompanied by a jumpwise change in entropy, and the GN2–GN3 transition by a continuous change in entropy. The increase in the entropy associated with the GN1–GN2 transition is $5.7 \pm 0.3 \text{ J mol}^{-1} \text{ K}^{-1}$ which is very close to the value of $R \ln 2$, suggesting that this transition is of the order–disorder type. The experimentally obtained value of ΔS is a superposition of two main contributions: the orientational contribution ΔS_o and the contribution ΔS_V related to a change in volume. This allows us to assume that ΔS can be written in the form

$$\Delta S = \Delta S_o + \Delta S_V. \quad (2)$$

The latter contribution ΔS_V for the first-order phase transition can be estimated from the relation

$$\Delta S_V = (\alpha/\beta)\Delta V_{12} \quad (3)$$

where α is the volume thermal expansion coefficient, β is the volume compressibility and ΔV_{12} is the change in volume at the phase transition. The contributions from equation (2) will be analysed further in this work.

The transition entropy of the GN2–GN3 transition is $1.5 \pm 0.3 \text{ J mol}^{-1} \text{ K}^{-1}$. This value seems to be too small for pure order–disorder transformation.

3.2. X-ray powder diffraction study

A small thermal anomaly observed in the calorimetric measurements in the vicinity of 384 K proves that GN crystals undergo a transformation to the third structural form. The existence of a new phase of GN has been confirmed by an x-ray diffraction study. A typical diffraction pattern of the GN2 phase obtained at 322 K is shown in figure 3(a) whereas the diffraction pattern of the GN3 phase recorded at 393 K is shown in figure 3(b). The most profound differences between them are seen for the reflections recorded for angles Θ of 8.5° , 11.8° and 17.2° . For GN2 these reflections are clearly double. With increasing temperature, their two components approach each other and overlap and, above 384 K, only single reflections are observed, which is illustrated in figure 3(b). The observed changes in diffraction pattern indicate a change in the crystal structure and confirm the continuous character of the GN2–GN3 transition.

3.3. Dilatometric studies at ambient and high pressures

As has been mentioned in section 1, the GN1–GN2 transition is accompanied by profound changes in the crystal shape. A typical course of the temperature changes in the specific volume of the crystal is presented in figure 4. It is clearly seen that the observed change in the crystal volume at the transition is negative and its magnitude,

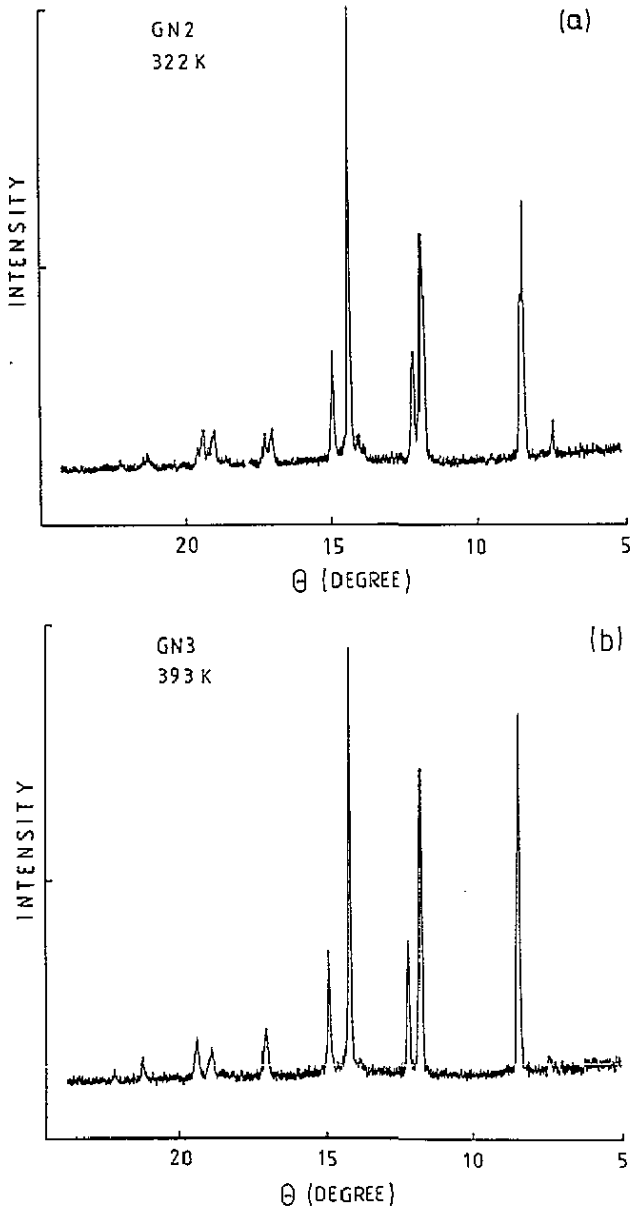


Figure 3. Diffraction patterns of the GN crystal for the phases (a) GN1 and (b) GN2.

$\Delta V_{12}/V_1 = -(1.85 \pm 0.05)\%$, was obtained as the average of three cycles of measurements by approximating the linear fragments of the $V(T)$ dependences up to the temperature T_{12} . The large temperature hysteresis of the abrupt changes in the specific volume related to the GN1–GN2 transition is shown in the inset. The vertical arrow in figure 4 indicates the temperature at which DSC measurements reveal a new thermal anomaly. At this temperature a slight anomaly has also been observed in the course of the $V(T)$ dependence. The change in volume at 487 K shown in figure 4 is related to the melting of the GN crystal. This

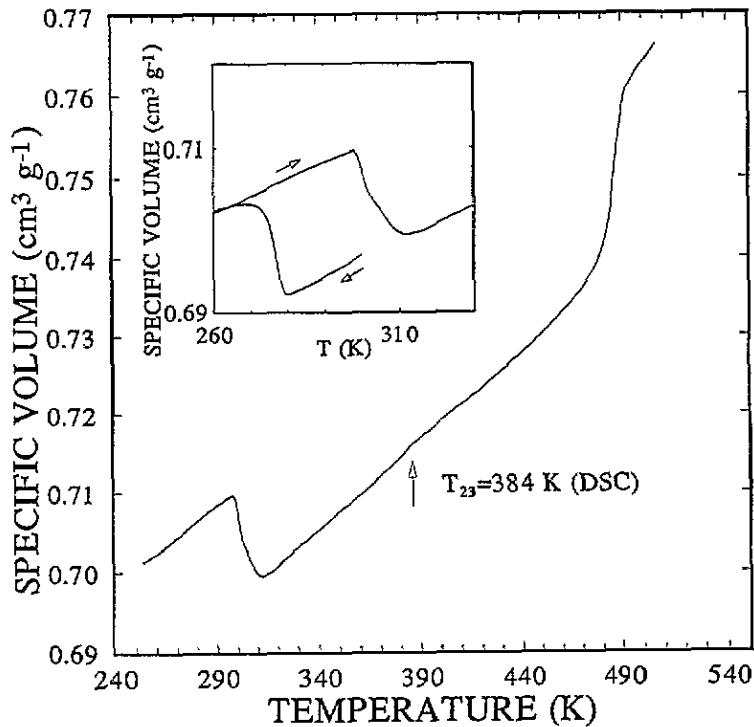


Figure 4. Temperature dependence of the specific volume of the GN crystal; the temperature was changed at a rate of 2 K min^{-1} .

process is accompanied by a 2.7% increase in volume.

The influence of hydrostatic pressure on the GN1–GN2 phase transition was analysed on the basis of measurements of specific volume as a function of temperature under a few different pressures. The results of these measurements are shown in figure 5 which also illustrates the way that the temperature T_{12} was determined. The main effect caused by a high hydrostatic pressure is a shift of the phase transition point towards lower temperatures. The p – T phase diagram shown in figure 6 indicates that, within the range of pressures studied, the temperature T_{12} linearly decreases with increasing pressure which can be expressed as

$$T_{12}(p) = T_{12}(0) + kp \quad (4)$$

where $T_{12}(0) = 298.5 \pm 0.4 \text{ K}$ is the phase transition temperature at ambient pressure and $k = -(24.3 \pm 0.8) \text{ K kbar}^{-1}$. The high absolute value of k proves the strong effect of pressure on the GN1–GN2 transition. The value of this coefficient can be helpful for an independent determination of the transition enthalpy and entropy from the Clausius–Clapeyron equation

$$dT_{12}(p)/dp = \Delta V_{12} T_{12}(0)/\Delta H_{12}. \quad (5)$$

Substituting appropriate numerical values into equation (5) we obtain $\Delta H_{12} = 1.97 \pm 0.08 \text{ kJ mol}^{-1}$ and $\Delta S_{12} = 6.58 \pm 0.03 \text{ J mol}^{-1} \text{ K}^{-1}$. The values calculated from the Clausius–Clapeyron equation are slightly higher than obtained directly from the calorimetric measurements. This discrepancy may be, among other factors, due to too high a value of ΔV_{12} estimated from our dilatometric measurements. The studies performed for a single crystal in the vicinity of the GN1–GN2 transition [10] have proved that the length of the

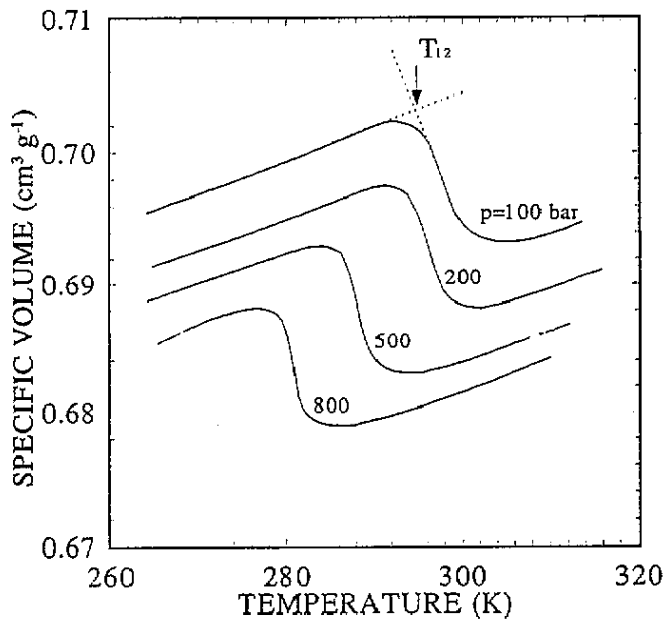


Figure 5. Specific volume of the GN crystal as a function of temperature in the vicinity of the GN1-GN2 phase transition at several pressures (heating rate, 2 K min⁻¹).

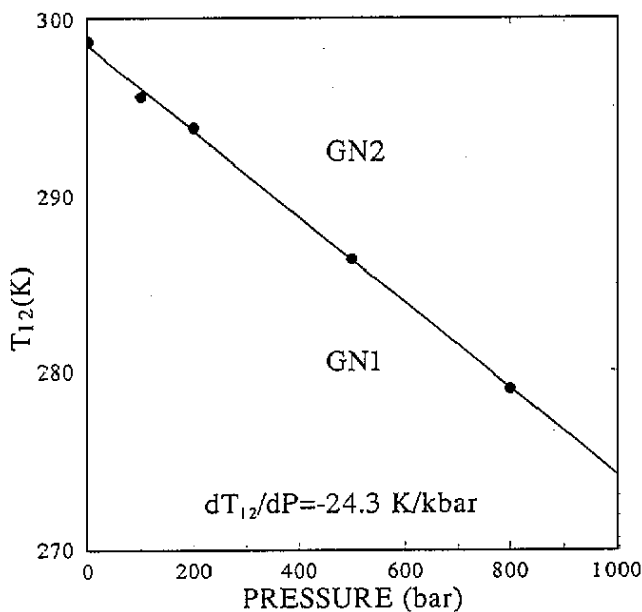


Figure 6. p - T phase diagram of the GN1-GN2 phase transition.

crystal needle increases jumpwise at T_{12} and then, for about 10 K after the transition, non-linear changes in the crystal dimension have been observed. This effect may be related to the presence of overheated or overcooled microregions in the crystal but it may also

reflect non-linear changes in the parameters of the unit cell near the phase transition. In the latter case the value of ΔV_{12} determined in the above-described way will be higher than the jump change in the crystal volume associated with the phase transition only, which can explain the observed discrepancy in the values of transition enthalpy and entropy found by the different methods. However, the solution to this question requires further detailed investigation and in particular structural studies in the vicinity of the GN1–GN2 transition.

To be able to estimate the contribution to the transition entropy related to the volume change ΔV_{12} we have to know the coefficients α and β occurring in equation (3). The coefficient of volume thermal expansion was determined from the temperature measurements of specific volume under atmospheric pressure (figure 4) to have a value of $\alpha = 3.2 \times 10^{-4} \text{ K}^{-1}$. The results of dilatometric measurements obtained for a few pressures permitted us to estimate the volume compressibility coefficient as $\beta = 2 \times 10^{-10} \text{ Pa}^{-1}$. Substituting the obtained values of α and β into equation (3) and assuming that $\Delta V_{12} = -1.60 \text{ cm}^3 \text{ mol}^{-1}$, we obtained $\Delta S_V = -2.6 \text{ J mol}^{-1} \text{ K}^{-1}$. This result indicates that ΔS_V gives an essential contribution to the total transition entropy. Knowing the estimated value of ΔS_V , we can find from equation (2) the orientational contribution $\Delta S_o = 8.3$ or $9.1 \text{ J mol}^{-1} \text{ K}^{-1}$ using the value of transition entropy from DSC or the Clausius–Clapeyron relation, respectively. Both values are close to $R \ln 3$. On the assumption that the GN1 phase is fully ordered, the orientational part of the excess molar entropy indicates the possibility of threefold disordering in the GN2 phase. However, the question remains whether the change in entropy at T_{12} can be attributed to a static disorder or dynamic process. As the above-discussed transition has not been observed in an NMR investigation of the GN crystal [4], we can conclude that the GN2 phase disorder cannot be related to the hydrogen movement in the N–H...O bonds as well as guanidinium ion movement which is connected with the proton movement. So, the possible dynamic disordering of the GN2 structure may arise only as a consequence of disordering of NO_3^- anions. The orientational disorder of the NO_3^- ions has been observed as a common feature in the structure of several simple nitrates [19–22].

3.4. Isotope effect on temperatures of phase transitions

To gain better insight into the mechanism of the phase transitions observed, we have undertaken studies to check the influence of deuterium substitution in the GN crystal on its physical properties. The degree of deuterium exchange in the DGN crystal was estimated from IR spectra to be 65–70%. Typical DTA runs recorded for GN and DGN crystals are shown in figure 7. As follows from a comparison of these data, the isotopic shift in the temperature of phase transitions is small. Taking into account the accuracy of determination of the phase transition temperature, we found no significant differences between the temperature T_{23} for GN and DGN crystals. In the case of the GN1–GN2 transition, T_{12} slightly increases as a consequence of the crystal deuterization. The average isotopic shift ΔT_{12} determined from a few cycles of measurements carried out for a few different samples is 3.6 K. A small isotopic effect indicates, similarly to NMR results, that the observed transitions are not related to the movement of protons in the N–H...O hydrogen bonds. Such a process is usually very sensitive to H isotopic exchange. The hydrogen bonds in the GN crystal are probably relatively long, similar to the situation in most other simple guanidinium salts [11–14]; so the protons remain ordered as they rest in deep potential wells. The shift in T_{12} towards higher temperatures suggests that deuterium substitution for hydrogen makes it more difficult to induce disordering in the DGN structure.

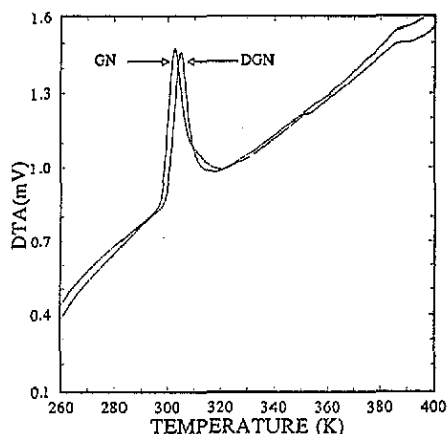


Figure 7. DTA curves for the GN and DGN crystals obtained on heating at a rate of change in temperature of 4 K min^{-1} .

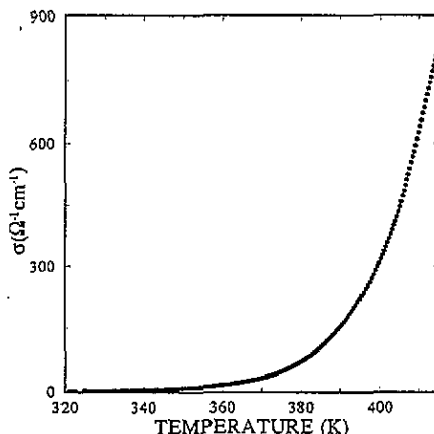


Figure 8. Electric conductivity of a polycrystalline sample of the GN crystal as a function of temperature.

3.5. Electric conductivity

The increase in the dielectric constant of the GN crystal reported in [10] and observed for temperatures above 320 K points to an increase in dielectric losses in this crystal with increasing temperature. The losses are due to increased electric conductivity. A typical course of the temperature changes in electric conductivity for a polycrystalline sample is shown in figure 8. The observed increase in conductivity may be attributed to the temperature-induced formation of lattice defects endowed with a charge. Both the formation and the motion of such defects can be expected to be activated processes. In such a case the temperature dependence of σ can be expressed by

$$\sigma(T) = \sigma_0 \exp(-\Delta E/kT) \quad (6)$$

where σ_0 is a constant and ΔE stands for the activation energy. By fitting equation (6) to a few courses of $\sigma(T)$ we determined the mean value of the activation energy as $\Delta E = 80 \pm 10 \text{ kJ mol}^{-1}$.

It is highly probable that the lattice defects are formed as a result of the breaking of the hydrogen bonds $\text{N-H} \cdots \text{O}$. This process seems to be easier in the disordered GN2 phase, in which the onset of the increase in electric conductivity is observed.

4. Concluding remarks

The application of several complementary methods of measurements permitted us to obtain new information about physical properties of the GN crystal. In particular, a new high-temperature phase of the crystal existing above 384 K has been detected. The present state of knowledge on the GN2–GN3 phase transition is, however, far from complete. Many more data are available on the GN1–GN2 phase transition. The change in entropy accompanying this transformation evidently proves that it is of the order–disorder type. Despite this disordering, the GN2 structure is more densely packed than the GN1 phase. The planar anions and cations bonded through a two-dimensional network of hydrogen bonds form a layered structure of the GN1 phase [16]. It seems that the essential structural changes accompanying the GN1–GN2 phase transition may be related to an abrupt change in the arrangement of the neighbouring layers which could explain the profound anisotropic changes in the GN crystal

shape observed earlier [10]. A similar phenomenon has been observed in the chain structure of 1,3-cyclohexanedione [23,24].

The layered internal structure of the crystal usually implies a strong anisotropy of its physical properties such as thermal expansion or compressibility. In particular, different influences of pressure can be expected in the directions parallel and perpendicular to the molecular layers. One of the expected effects induced by pressure in the GN crystal structure is shortening of the hydrogen bonds which strengthens the binding of the anions and the cations, hindering their disordering and/or rearrangement. On the other hand, owing to the high pressure the neighbouring layers in the crystal become closer to each other, which results in an increase in electrostatic interactions between them. The decrease in the phase transition temperature at elevated pressures indicates that the interlayer electrostatic interactions dominate and decide the mechanism of the observed transition. The minor importance of hydrogen bonds has been confirmed by the slight H isotope effect. An increase in the electrostatic interactions in the GN crystal leading to the appearance of the phase transition can be achieved by increasing either the temperature or the pressure.

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