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A detailed IR study of the order–disorder phase transition of $NaNO_2$

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Abstract

The infrared spectra of sodium nitrite $NaNO_2$ have been investigated between 400 and 4000 cm^{-1} over a wide range of temperature (27–250°C). The results are reported during the order–disorder phase transition (II→I) at temperature about 161°C. The study includes spectral analysis and interpretation of band shape, peak height, band width and band intensities of the internal modes of vibrations as functions of temperature. The present results strongly confirm the phase transformation process from the ordered state II to the disordered state I of $NaNO_2$ by clear variations obtained in the spectral parameters for the bending modes ν_2 ($\approx$830 cm^{-1}) asymmetric stretching mode ν_3 ($\approx$1270 cm^{-1}) and combination mode ($\nu_1 + \nu_3$) ($\approx$2552 cm^{-1}).

The rotational energy barrier for the nitrite group NO_2 is determined for both ordered and disordered phases using ν_2 and ν_3 modes. Also, the phase transition process is found to be activated by an energy of 0.16 eV in the regions of these two modes.
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1. Introduction

Sodium nitrite is a compound that has a phase transition temperature at about 162°C. Above this temperature, the crystal structure is non-polar and belongs to the orthorhombic system. Its space group is D_{2h}^{25}-Immm [1]. Below the transition temperature, the structure is still orthorhombic but is polar along the *b*-axis and its space group being C_{2v}^{2s}-Immm [2].

A considerable amount of experimental and theoretical work has been carried out on the ordered and disordered phases of sodium nitrite $NaNO_2$ following as the electrical [3], spectroscopic [4,5] and structural [6] properties over a wide temperature range. The permanent dipoles of the $NaNO_2$ radical in the ordered phase (ferroelectric phase) below the phase transition point are aligned parallel to the spontaneous polarization along the *b*-axis. In the disordered phase (paraelectric phase) beyond higher than the phase transition point, the NO_2^-radicals point to be ± *b*-directions [7].

Although the phase transition phenomenon in $NaNO_2$ has been intensively studied, there are many contrary statements in the literature since there is an additional anomalies at 100°C [8] and at 178°C [9,10]. It was also reported that the character of the $NaNO_2$ phase transition is closed to the second order kind [11] and not of the first order one [7,9].

On the other hand, some authors reported that the rotation of the NO_2^-radicals takes place around *c*-axis [1,12] or around *a*-axis as reported by the authors [10,13]. But the studying of the phase transition in $NaNO_2$ in the high frequency range using spectroscopic analysis is not clearly reported. Thus, the purpose of this investigation is to study in detail the

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infrared (IR) spectrum of $NaNO_2$ in both ordered phase II and disordered I between room temperature (27°C) and (250°C) below the melting point (270°C). Also, one of the fundamental aims in the interpretation of the IR spectroscopic data of $NaNO_2$ is to determine the nature and extent of ordering and disordering in the two phases II and I.

2. Experimental

IR spectra were recorded using a Perkin-Elmer 1600 a FT–IR spectrophotometer and the experimental techniques employed were essentially identical to those described previously [14]. The materials used were ultra pure $NaNO_2$ obtained by the British Drug House (B.D.H.) Laboratory Chemical Division, England. The samples contained 2 mg mixed with about 200 mg powder of KBr and placed in a cylindrical die of 10 mm diameter after shaking the mixture for about half a minute. The die was evacuated to insure dryness and the sample was then pressed under pressure of about 620 kg/cm^2. A disc of approximately 1 mm thick was obtained. The sample temperature was measured to an accuracy of ±1°C. The spectrum was recorded in the region 400–4000 cm^{-1} by computerized system attached to monitor and printer.

3. Results

In interpreting the IR adsorption we use Herzberg's notations [15] for the internal fundamental normal modes of vibrations of NO_2 in which ν_1 denotes the totally symmetric N–O stretching mode, ν_2 is the bending mode and ν_3 is the asymmetric mode.

3.1. Temperature dependence of the bands in $NaNO_2$

In the present study, the observed room temperature spectrum of $NaNO_2$ did not exhibit any bands which could be attributed to any mode other than those due to ionic fundamental of the $NO_2{}^-$ group. The accuracy of frequency measurements is calculated as ±3 cm^{-1} for sharp peaks and ±10 cm^{-1} for broad bands. IR spectra were measured at, room temperature (RT) (27°C), 91, 112, 131 and 151°C for the ordered phase II (low temperature phase) and at temperatures 180, 205, 225 and 250°C for the disordered phase I (high temperature phase). The frequencies of the bands for the two phases are collected in Table 1.

Fig. 1 shows one example of the IR spectra in the ordered phase II at 27°C (room temperature ordered phase) and in the disordered phase I at 225°C. Also in the intermediate state at temperature 161°C. It can be easily noticed that there is a slightly change in the mode frequencies during the transformation to the different states. Also, there is a remarkable variation in the band width and the peak heights of the different modes. For a detailed investigation, three important modes were selected and studied as the temperature of the samples increased from room temperature (RT) 27°C up to 225°C as shown in Fig. 2. These three modes were ν_2 ($\approx$830 cm^{-1}), ν_3 ($\approx$1270 cm^{-1}) and the combination mode ($\nu_1 + \nu_3$) $\approx$2552 cm^{-1}. They were found to be sensitive to ordering and disordering states. As shown in Fig. 2, the three modes subjected to a clear change in the half band width and peak height during the elevation of the temperature. It was noticed that, the variation in peak height and band width increased in phase II, while this variation decreased in phase I.

3.2. Detection of the phase transition II→I of $NaNO_2$

The variation of the half band width $\Delta\nu_{1/2}$ of the three modes ν_2, ν_3 and the combination mode ($\nu_1 + \nu_3$) are shown in Fig. 3. For the asymmetric mode ν_3 which showed itself as a broad band centred at $\approx$1270 cm^{-1} (at RT), the change in the band width showed a broad peak at 161°C. But for the bending mode ν_2 at 830 cm^{-1} and the combination mode ($\nu_1 + \nu_3$) at $\approx$2552 cm^{-1}, a little broadening could be observed in the same temperature range. This variation in the band width of the three modes are consistent with one another which clearly indicates a probable change in the phase state.

The variation of the peak height of the three modes ν_3, ν_2 and ($\nu_1 + \nu_3$) are shown in Fig. 4. One can see that as the temperature increases up to 130°C the slight change in peak height (Ph) increases up to 161°C and give a maximum change in ν_3, ν_2 and ($\nu_1 + \nu_3$). This strongly supports what is observed before. Fig. 5 shows the variation take place in peak intensity of the principle modes ν_3, ν_2 and combination ($\nu_1 + \nu_3$). The intensity variation of the ν_3 mode showed a maximum value at 161°C, also the ν_2 mode and the

Table 1
Infrared spectra of $NaNO_2$[a]

Frequency assignment (cm^{-1})	Order phase II												Transition point		Disordered phase I							
	27°C		70°C		91°C		112°C		131°C		151°C		161°C		180°C		205°C		225°C		250°C	
	ν	T^* (%)	ν	T^* (%)	ν	T^* (%)	ν	T^* (%)	ν	T^* (%)	ν	T^* (%)	ν	T^* (%)	ν	T* (%)	ν	T^* (%)	ν	T^* (%)	ν	T^* (%)
ν_2SP	830	70	830	63	830	56	832	71	830	59	830	51	833	56	830	64	828	83	829	73	828	72
ν_3BB	1270	3	1270	4	1268	2	1269	4	1273	14	1266	6	1264	8	1270	5	1275	16	1265	5	1261	8
ν_1SH	1383	52	1382	37	1383	36	1383	42	1383	45	1385	36	1380	31	1382	37	–	–	1384	42	1383	33
$2\nu_2$SH	1640	–	1636	66	1650	68	1632	68	1630	67	–	–	1645	66	1637	70	–	–	1652	62	1647	54
$(\nu_1 + \nu_3)$ BB	2552	27	2549	74	2554	76	2555	79	2554	73	2543	77	2555	69	2546	78	2562	78	2548	66	2558	60

[a] T^*: Transmission; ν: wave number (cm); SP: sharp peak; SN: shoulder; BB: broad band.

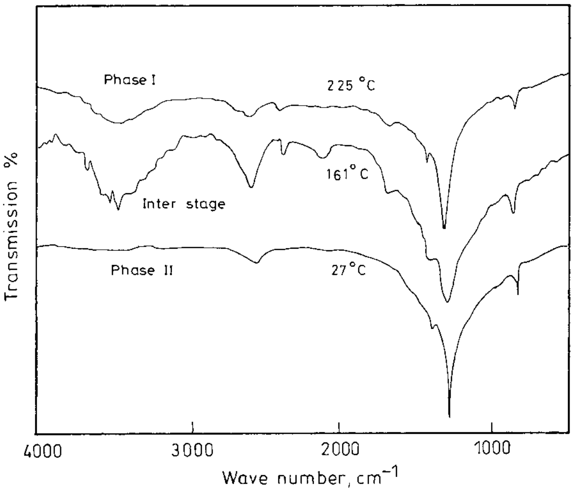

Fig. 1. Infrared spectra of $NaNO_2$ for the two phases I, II and the intermediate stage.

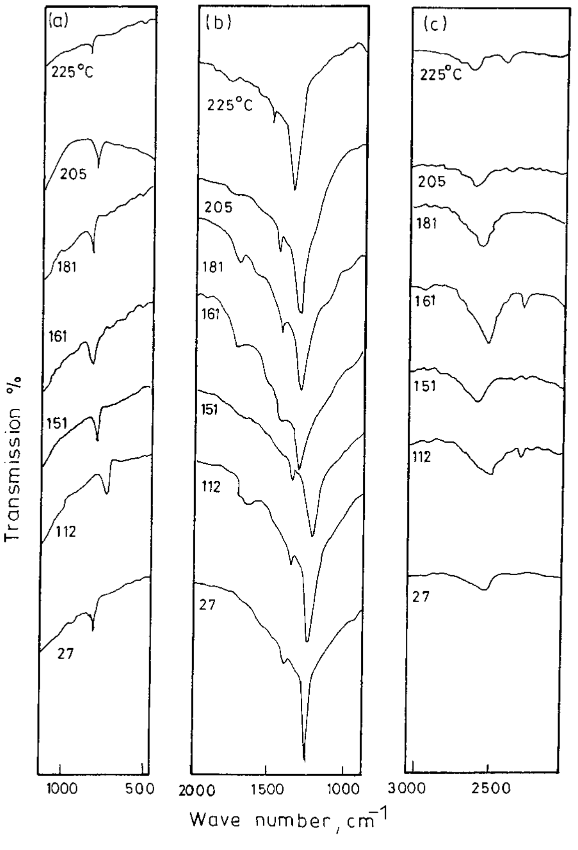

Fig. 2. Detailed contour variation of the modes (a) ν_2 (≈830 cm^{-1}); (b) ν_3 (≈1270 cm^{-1}); and (c) combination ($\nu_1 + \nu_3$) (≈2552 cm^{-1}) for $NaNO_2$ samples during the phase transition II→I.

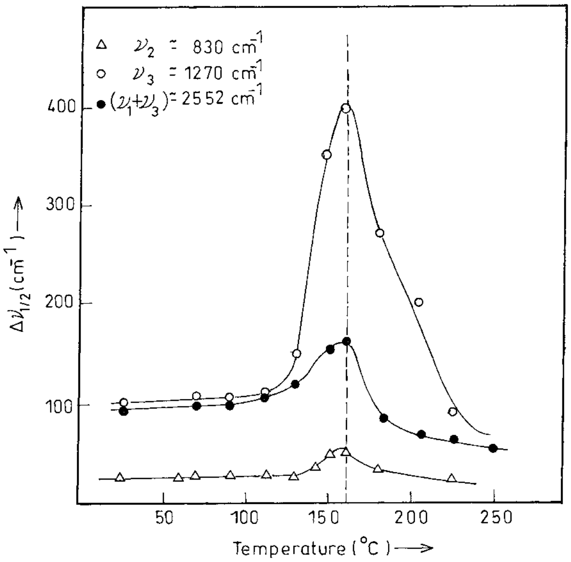

Fig. 3. Variation of half band width $\Delta\nu_{1/2}$ with temperature for the modes ν_2, ν_3 and ($\nu_1 + \nu_3$).

combination ($\nu_1 + \nu_2$) showed the same behaviour. One can easily see that the band width, relative peak height and the peak intensity for ν_2, ν_3 and combination ($\nu_1 + \nu_3$) modes showed anomalous character during the phase transformation process.

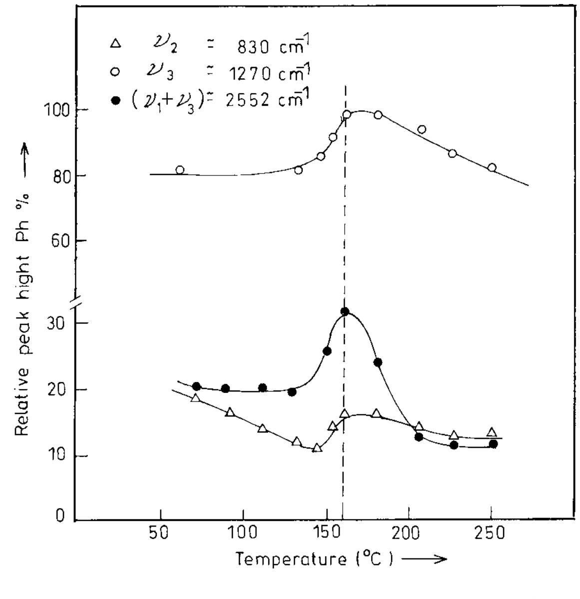

Fig. 4. Temperature dependence of relative peak height Ph for ν_2, ν_3 and ($\nu_1 + \nu_3$) modes during the phase transition II→I of $NaNO_2$.

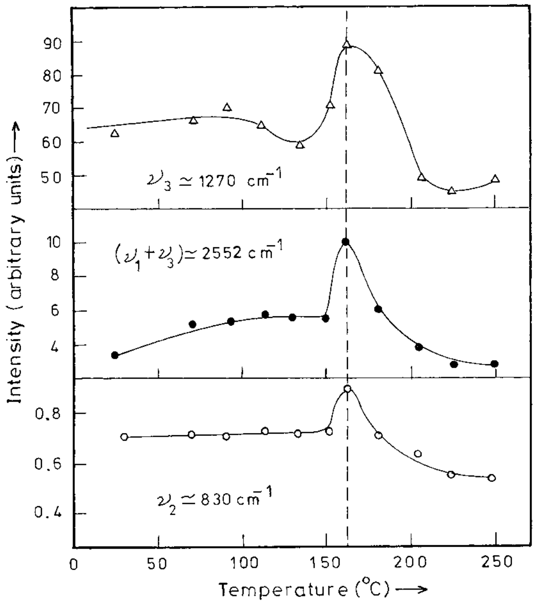

Fig. 5. Variation of IR band intensity with temperature for modes ν_2, ν_3 and combination ($\nu_1 + \nu_3$).

3.3. Determination of the rotational energy barrier

The energy barrier separating the different orientations of the NO_2^- group in the two phases I and II is determined using the relaxation time equation [16].

$$\tau = \tau_0 \exp\frac{E}{kT}$$

where E is the rotational energy barrier, k the Boltzman constant and T the absolute temperature.

On the other hand, the relaxation time was determined by the equation [17].

$$\tau = \frac{1}{\pi}\Delta\nu_{1/2}c$$

where $\Delta\nu_{1/2}$ is the half band width of the IR absorption band and c the velocity of light. The results of these calculations in the two regions of ν_2 and ν_3 (as shown in Fig. 6) indicate that for ν_2 band, phase I was associated with an energy barrier of 0.27 while phase II was associated with an energy barrier of 0.43 eV. These two values of energies becomes 0.41 and 0.57 eV, respectively, in the region of ν_3 band. It is clear that from the above results the phase transition process in the two regions of ν_3 and ν_2 is activated by an energy 0.16 eV.

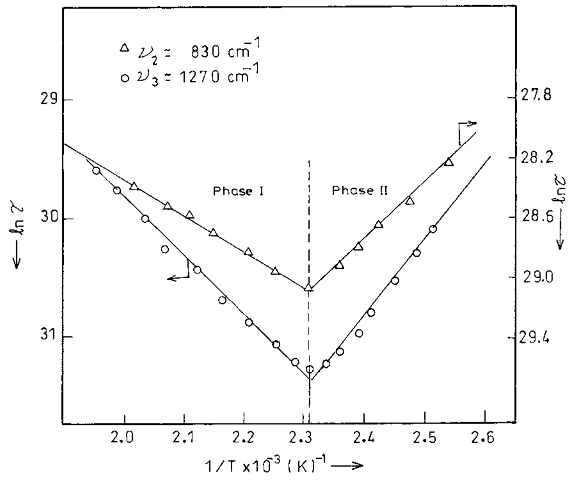

Fig. 6. Temperature dependence of the relaxation time in the region of the two modes ν_2 and ν_3.

4. Discussion

The phase transition is considered to be as interruption of the thermodynamic functions characterizing the state of a substance at a special point called the phase transition point [18]. As soon as such a point is reached the initial phase can no longer exist and changes to a new phase. At this critical point a substance gains abnormal properties or acquires unusual behaviours. The phenomenon of ordering–disordering of molecules in $NaNO_2$ crystals may be experimentally observed by studying the temperature dependence of the vibrational spectra in both states. This can be done in the region of the internal and external lattice modes of vibrations of $NaNO_2$ molecules. Increasing the temperature, specially near the phase transition point, the possibility of reorientations of the molecules considerably increases. The character of reorientation changes qualitatively at the phase transition point and in turn, this should lead to variations in the characteristics of the vibrational spectra of $NaNO_2$.

According to the above consideration, it was thought reasonable to study in the present work the spectroscopic effects related to the processes of ordering and disordering, principally by studying the IR absorption spectrum of NO_2^- ions. Also, the effect of temperature on the IR absorption spectra gave important information about the dynamics of the processes of disordering which lead to some understand of the nature of the order/disorder phenomena in sodium nitrite.

In the present work, the IR spectra of $NaNO_2$ compound has been precisely measured in the region between 400 and 4000 cm^{-1} where only the three fundamental internal modes of vibrations (v_2, v_3 and v_1), the combination mode ($v_1 + v_3$) and the first overtone ($2v_3$) of the $NO_2{}^-$ radical will be taken into account for the study of phase transition. These fundamental modes of vibrations are the symmetric bending mode v_2 ($\approx$830 cm^{-1}), asymmetric stretching mode v_3 ($\approx$1270 cm^{-1}) and symmetric stretching mode v_1 ($\approx$1383 cm^{-1}).

It is well known that a characteristic shape of an absorption band for a distinct molecule is related to the number of ions that undergo, the various energy transitions.

Beside the fundamental modes v_2 and v_3, the combination mode ($v_1 + v_3$) observed here at $\approx$2552 cm^{-1} also was found to be sensitive to the ordered and disordered states of the nitrite group in $NaNO_2$.

The intensity of each line depends on the number of ions undergoing a certain energy transition and the band envelope as a whole is a representation of the total number of ions involved [19] as previously shown in Fig. 5. As the temperature of the ions increased the contour of the absorption band (and in turn the area under the envelope) will increase, provided that the increase in temperature increase also the number of the $NO_2{}^-$ ions initially being in the vibrational level $v = 0$.

In order to explain the reduction of intensity of v_2, v_3 and the combination ($v_1 + v_3$) modes as shown in Fig. 5, it is proposed that the $NO_2{}^-$ ions are oriented in a disordered fashion among the positions with nearly equal energies and symmetry [20]. Due to thermal agitation of the system the rate of orientation among these positions increases with temperature which reflected as a decrease in the band intensities of v_2, v_3 and combination ($v_1 + v_3$). The degree of disordering of anions in the region of the phase transition II→I could be controlled by the rates of increase of the band intensities of modes under investigation. All IR spectra of $NaNO_2$ obtained in the present work are characterized by the presence of a broad band v_3. This strong broadening of the inhomogeneity band is due to the difference between the orientation action of the individual $NO_2{}^-$ ions.

The asymmetry in the IR band shape of the mode v_2 $\approx$830 cm^{-1} could arise from the combination of the lattice mode [21] or from the coupling of the vibrational modes of $NO_2{}^-$ groups, or due to isotopically different forms of the $NO_2{}^-$ ions [22].

One can see that the phase transition II→I cause a gradual increase of the broadening of the v_3 band in the ordered phase II, then followed by a gradual reduction in the disordered phase I as shown in Fig. 2. This may be attributed to the fact that, transformation of $NaNO_2$ (phase II) to the high temperature phase I imply sufficient oscillation of the anions to unlock the 0 atoms from their cation coordination [20]. The same behaviour was observed also in the vibration mode v_2 and combination ($v_1 + v_3$) (see Fig. 2).

The ordered phase II of $NaNO_2$ differs from the disordered phase I by the greater hindrance of the motion of the $NO_2{}^-$ ions [23] and confinement of the reorientations solely to the plane of the ion. If we assume these ions are in different local field, we can give an account for the origin of the high frequency side of the band. The increase in temperature destroys the correlation of neighboring ions. The reorientational motion of the $NO_2{}^-$ ions between two equivalent positions existing in phase II was responsible for the large width of the investigated bands near the phase transitions point. Further increase in temperature caused a large reduction of the band width specially for the mode v_3 and combination ($v_1 + v_3$) as shown in Fig. 3.

According to the present study the peak height of IR bands of $NaNO_2$ increases with temperature in ordered phase II and decreases in the disordered phase I (as clear from Fig. 4). To interpret such a behaviour, it is well known that below the phase transition temperature point (161°C) the structure of $NaNO_2$ is belonged to body centered orthorombic and is polar along the *b*-axis and its space group is being C_{2v}^{2s}-Immm. But above 161°C, the crystal structure is nonpolar and still belongs to the orthorhombic system. Its space group is being D_{2r}^{25}-Immm. Such changes accompanying the transformation from lower symmetry for the unit cell to a higher symmetry are responsible of such behaviour. The height of the potential barrier E of the ordered phase II was found to be 0.43 eV, while that for the disordered phase I was found to be $'E = 0.27$ eV in region of v_2 band. The corresponding values of energies in the region of v_3 band becomes

0.57 and 0.411 eV, respectively. Both E and E' represent the potential energy which must be crossed during the reorientation process. In fact the complete disordering of the NO_2^- radical, occurring at a critical temperature $T = 161°C$ causes a loosening of the ionic bonds [24]. This effect tends to reduce the height of the energy barrier.

The value of $\Delta E = E - E'$ represents the activation energy required to perform the order–disorder phase transition process. According to the present work ΔE is found to be 0.16 eV in the regions of the two modes v_2 and v_3. The ordered state of the NO_2^- ions in the lattice existing at a temperature below the phase transition temperature 161°C.

However, the orientations of the nitrite group are separated by a potential barrier of about 0.43 and 0.57 eV in the ordered phase II and 0.27 and 0.411 eV in the disordered phase I in the regions of the modes of vibration v_2 and v_3, respectively. Increasing the temperature of $NaNO_2$ crystals leads not only to a thermal population of the alternative orientation but also decreases the depth of the potential well as mentioned before.

References

[1] K. Komatsu, K. Itoh, F. Nakamura, J. Phys. Soc. Jpn. 57 (1988) 2836.
[2] M.I. Kay, B.C. Frazer, Acta Crystal. 14 (1961) 56.
[3] S.A. Ahmed, M.H. Ali, Phys. Stat. Sol. (b) 194 (1996) 517.
[4] F. Brechat, B. Wyncke, J. Phys. C. (GB) 18 (8) (1985) 1705.
[5] Lo. Wen-Jui, M.-y. Shen, C. Yu, Y.-P. Lee, J. Chem. Phys. 104 (3) (1996) 935.
[6] M. Becci, E. Castellucci, Chem. Phys. 135 (1989) 363.
[7] Y. Yamada, I. Shibuya, S. Hoshino, J. Phys. Soc. Jpn. 18 (1963) 1594.
[8] K. Hamano, K. Negishi, M. Mazutake, S. Nomura, Jpn. J. Appl. Phys. 2 (1963) 83.
[9] N. Maruyama, S. Sawada, J. Phys. Soc. Jpn. 20 (1965) 811.
[10] E.V. Chister, M.S. Shur, Fiz. Tverd. Tela 9 (1967) 1015.
[11] H. Betsuyaka, J. Phys. Soc. Jpn. 27 (1969) 1485.
[12] M. Itoh, K. Kohra, Jpn. J. Appl. Phys. 18 (1979) 527.
[13] H. Vogt, H. Happ, Phys. Stat. Sol. (b) 44 (1971) 207.
[14] F. El-Kabbany, Y. Badr, M. Tosson, Phys. Stat. Sol. (a) 63 (1981) 699.
[15] G. Hertsberg, Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, Princeton, New York, 1966.
[16] Y.G. Frenkel, Kinetic Theory of Liquids Izd. Akad. Nauk SSSR, Moskva, 1959.
[17] G.P. Buyan, I.I. Kondilenko, V.E. Pogorelov, Soviet Phys. Optics Spectrosc. 27 (1962) 132.
[18] R. Brout, Phase Transition, Benjamin, New York, 1965.
[19] L.N. Alpert, E.W. Keisher, A.H. Szymask, Theory and Practice of Infrared Spectroscopy, Plenum Press, London, 1970.
[20] P.P. Mayer, J.J. Copponi, Acta Crystal. B38 (1982) 2543.
[21] R.A. Schroder, C.W. Weir, E.R. Lippincott, J. Res. Nat. Bur. Stand. 65 (1962) 407.
[22] M.H. Broker, D.E. Irish, Can. J. Chem. 48 (1970) 1183.
[23] J.L. Amoros, R.L. Banerjee, R. Soc. (Hist. Nature) 58 (1960) 165.
[24] Y.A. Badr, R. Kamel, J. Phys. Chem. Solids 41 (1980) 1127.