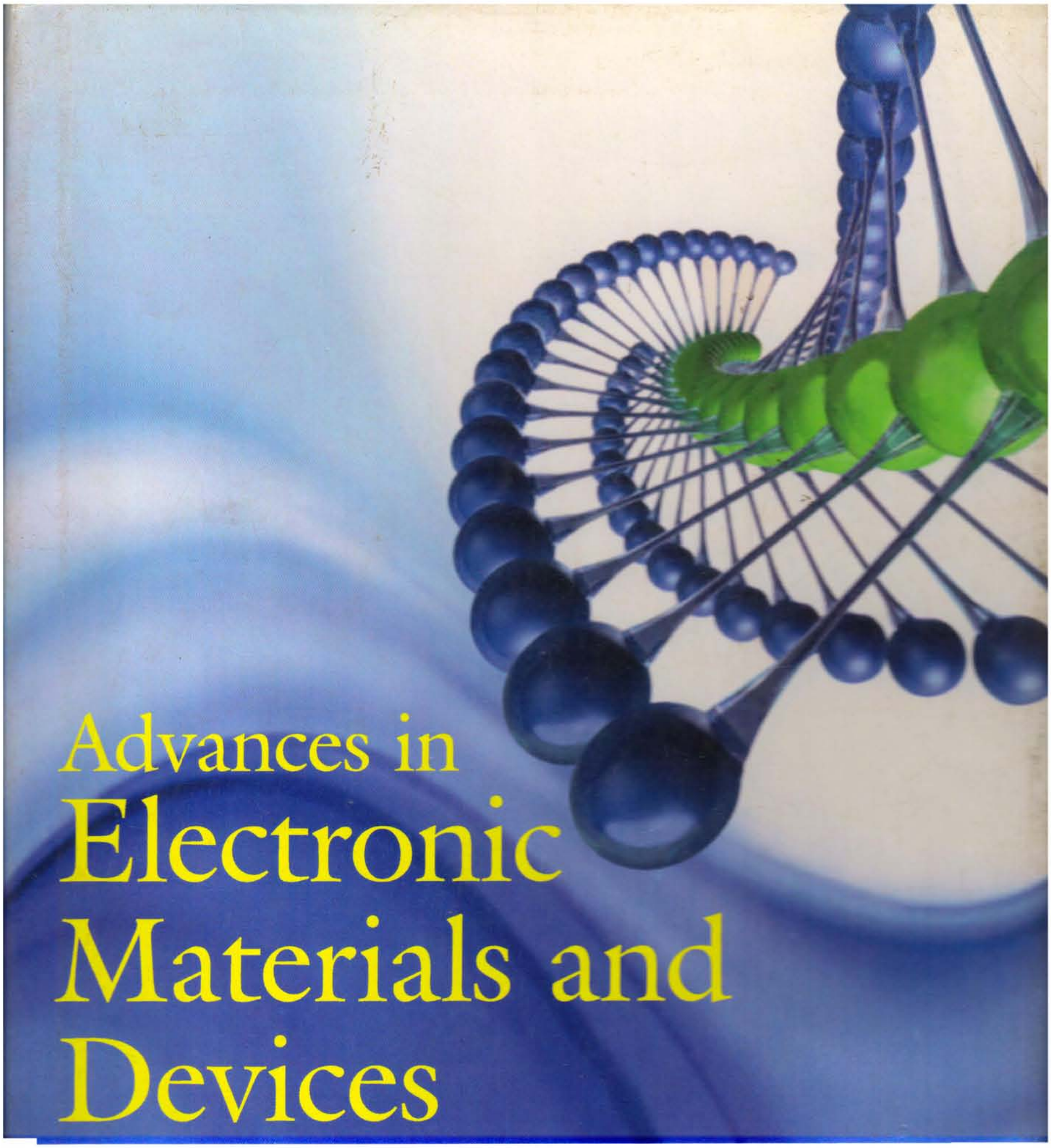

Advances in Electronic Materials and Devices

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Advances in Electronic Materials and Devices
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X-ray Structural Investigation on $(NH_4)_3H(SO_4)_2$ Single Crystal: Nature of H-bonds

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Abstract: Precise X-ray structural analysis on the single crystal of Triammonium Hydrogen Disulphate $(NH_4)_3H(SO_4)_2$ was carried out to study the structural details and the hydrogen bond (H-bond) character. The structural data so obtained are compared with other isomorphous crystals reported earlier. Room temperature lattice parameters observed are: a = 15.431(3) Å, b = 5.863(4) Å, c = 10.156(2) Å, β = 101.86(3)° and space group is C2/c with Z = 4. Neighbouring sulphate SO_4^{-2} ions are linked together in pairs by a H-bond, O·H···O with R_{O-O} distance 2.549 Å that is slightly larger than the critical H-bond distance showing that the H-bonds are weak. The positions of H-atoms could not be located directly from the structure refinement. However, the Fourier map used to obtain distortion in the electron density distribution around O_1 atom shows the H-bond formation. The structural distortion calculated from point charge model using the positional parameters of S and O atoms reveals that the tetrahedral SO_4^{2-} is mainly distorted along x-y plane. The statistical disorder or dynamical tunnelling effect in H-atoms could not be identified as the electron density distortion around H-bond is not sufficient to provide double minimum peak.

Keywords: $(NH_4)_3H(SO_4)_2$, Zero-dimensional hydrogen-bonded crystal, Single crystal X-ray diffraction, Structure analysis.

Introduction

Triammonium Hydrogen Disulphate $(NH_4)_3H(SO_4)_2$ (TAHS) belongs to the family of crystals having general formula $M_3H(XO_4)_2$ (M = K, Rb, Cs, NH_4 and X = S, Se). It is reported that $H(XO_4)_2$ dimer forms an isolated hydrogen bond (H-bond) and plays an important role as dipoler unit and further that these

substances have no proton network characteristic of traditional H-bonded crystals like KDP. Therefore, these H-bonds are characterised as zero-dimensional system. It undergoes a sequence of phase transitions and shows low temperature ferroelectric phase. Structural information based on XRD work are reported for different phases of pure TAHS [1], mixed crystals TRAHS (Rb/NH_4) with Rb concentration < 0.18 [2] as well as for isomorphous potassium and rubidium salts [3, 4]. The position of hydrogen atoms could not be identified in most of the XRD studies especially for phase II.

In the past, attempts have been made to study the orientational dynamics of NH_4 ions using neutron diffraction data [5]. The study suggests that both NH_4(I) and NH_4(II) are highly disordered and the nature of disorder is different along monoclinic plane and perpendicular to it. In isomorphous TKHS [3], it has been suggested that electron density distribution along the H-bond may get smeared out and asymmetric distribution is used for locating the double minima of H-atoms and to identify the nature of hydrogen disorder. Thus, the nature of H-bond and the dynamics of ammonium ions in these crystals are still not unambiguously understood in spite of several efforts. Therefore, the crystal structural analysis of TAHS is reported and the possible nature of H-bond is extracted from the result obtained.

Experimental Procedure and Structure Analysis

Hexagonal plate like single crystals of TAHS were grown by slow evaporation method from the aqueous solution of Ammonium Sulphate $(NH_4)_2SO_4$ (21.0 wt%) and Sulphuric Acid H_2SO_4 (7.0 wt%). Transparent specimens having single domain with clear optical axis were cut under a polarising microscope and shaped as a sphere with a diameter 0.35 mm. X-ray single crystal study is carried out using the Siemens P4 Single Crystal Diffractometer with MoKα radiation of wavelength 0.71073 Å with the X-ray power of 40 kV × 40 mA. The unit cell parameters were determined by least-squares refinement of 25 reflections with the diffraction angles $2\theta = 10 - 30°$. Intensity measurements were carried out in the ω-scan mode. The maximum 2θ in which intensity data were collected was 50.0°. The ϕ stepping rate is varied from 1.0 to 2.0 s^{-1} in the range $2 < 2\theta < 50°$ for $-1 \leq h \leq 9, -6 \leq k \leq 1, -10 \leq 1 \leq 10$ (max. $\sin\theta/\lambda = 0.8069$ Å^{-1}). Three standard reflections were monitored after every hundred reflections to check the stability of the measurements. After processing the raw data, Lorentz and polarisation corrections were made. No correction was made for absorption because the linear absorption coefficient is small for MoKα.

The obtained lattice parameters are: a = 15.431(3) Å, b = 5.863(4) Å, c = 10.156(2) Å, β = 101.86(3)°, V = 899.22(58) Å^3, $F(000)$ = 519.9 and μ = 0.619 mm^{-1}. The crystal is monoclinic with the space group C2/c. The calculated density, D_c (1.83 g/cm^3) agrees well with the measured experimental one, D_m = 1.826 g/cm^3. 596 measured reflections were averaged to 379 unique observed reflections $[F_0 > 4\,\sigma\,(F_0)]$; R(int) = 0.1095; $R(\sigma)$ = 0.0457. The function minimised was $\Sigma w(|F_0| - |F_c|)^2$, $w = 1/\sigma^2(|F_0|)$. Anisotropic displacement parameters were used for non-H-atoms and an isotropic parameter for the H-atom. The final values of R-factor and the weighted R-factor are 0.177 and 0.281, respectively. The two

discrepancy factors are defined as $R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$ and $R_w = \{\Sigma w(|F_0| - |F_c|)^2/\Sigma w(|F_0|)^2\}^{1/2}$, respectively. The calculations were performed using SHELXS-97 [6] and ORTEP-III [7].

Results and Discussion

The lattice parameters obtained in the present analysis agree well with the earlier reports. The positional parameter of Nitrogen in the present analysis reveals two sets of non-equivalent positions: one set (8-atoms in the unit cell, N_2) at general positions and the other 4 atoms (N_1) at special positions on two fold axes with four formula units. Thus, there should be 12 ammonium ions and 8 sulphate ions in the unit cell. Final positional parameters are given in Table 1 and bond lengths and angles for the sulphate group are given in Table 2. The crystal structure is shown in Fig. 1. The SO_4^{2-} tetrahedral shows slight distortion as revealed by the

Table 1. Atomic positions of the non-hydrogen atoms in $(NH_4)_3H(SO_4)_2$ at room temperature

Atom	x	y	z
N(1)	0.000000	0.266657	0.750000
N(2)	0.199231	0.724863	0.651104
S	0.115837	0.217779	0.461777
O(1)	0.019774	0.182197	0.445550
O(2)	0.147848	0.027641	0.397516
O(3)	0.148285	0.221195	0.604677
O(4)	0.128132	0.432746	0.399655

Table 2. Bond lengths and angles of SO_4 group in $(NH_4)_3H(SO_4)_2$ at room temperature

Bonds (Å)		Angles (°)	
S-O(1)	1.472	O(1)-S-O(2)	105.83
S-O(2)	1.430	O(1)-S-O(3)	104.43
S-O(3)	1.435	O(1)-S-O(4)	107.18
S-O(4)	1.439	O(2)-S-O(3)	113.02
		O(2)-S-O(4)	113.18
$R_{O(1)-O(1)''}$	2.549	O(3)-S-O(4)	112.40

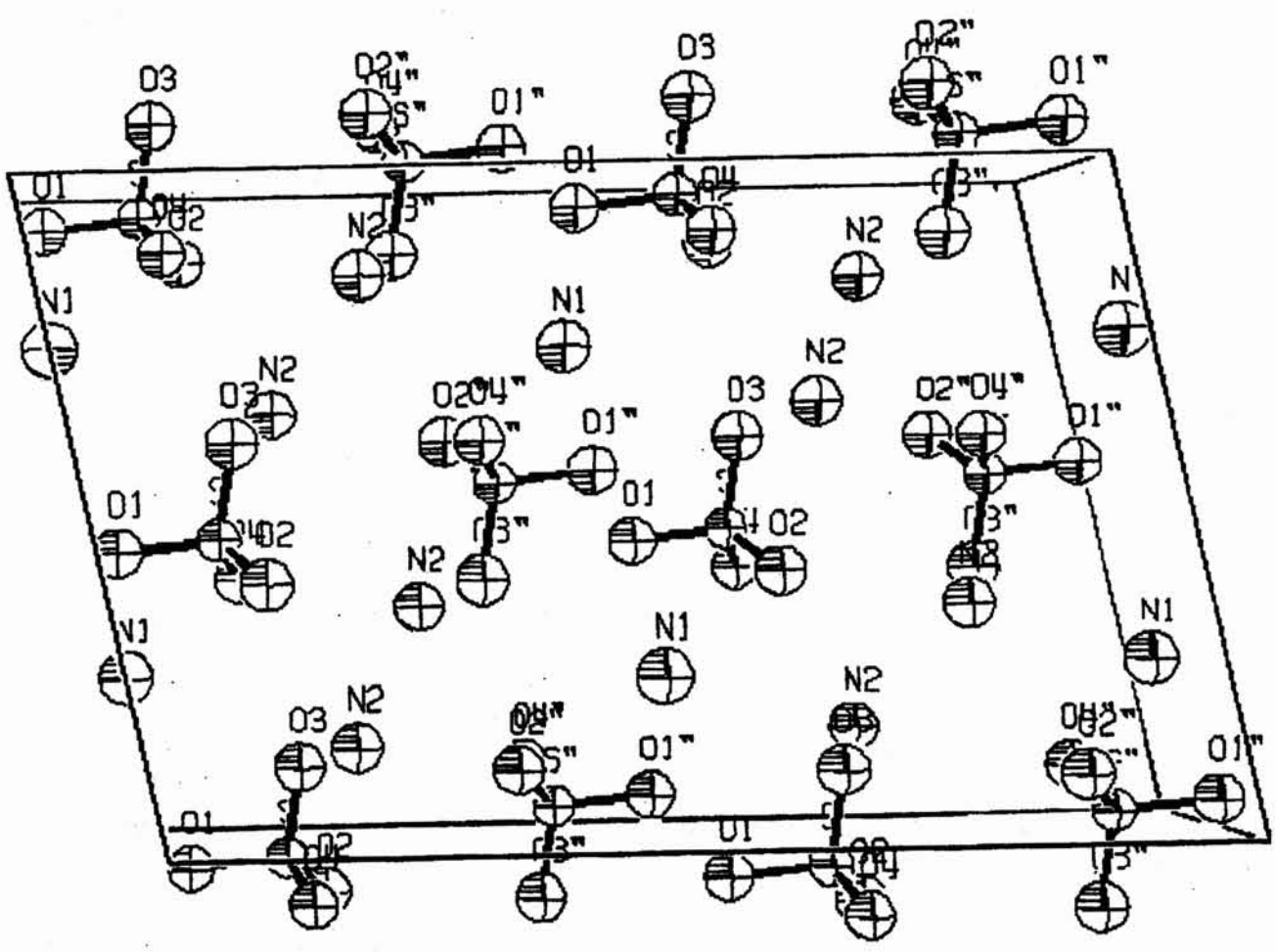

Fig. 1. The b-axis projection of the room temperature structure of $(NH_4)_3H(SO_4)_2$.

O-S-O bond lengths that are different for two bonds. In earlier studies, one S-O bond has been found elongated while three other bonds remained almost the same. In the present data, however, we find elongated bond length less than reported earlier and the three bonds slightly shorter than normal bond length (Table 2). In order to understand the nature of distortion that SO_4^{2-} tetrahedral undergoes, we calculated the structural distortion in the tetrahedral based on point charge model [8] using the positional parameter obtained in the present study. The values of δx, δy and δz are found to be 0.019309, 0.007337 and 0.00029 Å, respectively with δr being 0.020658 Å. This clearly shows that sulphate ion is not really elongated rather internal structure is distorted with dipole moment effectively remaining on xy-plane. This is possible if hydrogen atoms are disordered from the (0, 0, 0) and (0, 0, 1/2) positions. This means that each pair of neighbouring sulphate ions is linked by one hydrogen bond of type O-H...O. The positions of hydrogen atoms are located by using the model for hydrogen bond attached to oxygen atoms [9] and from this H-bonding is realised only between O_1-O_1'' with $R_{O\text{-}O}$ distance being 2.549 Å that is slightly larger than that reported earlier 2.540 Å. Further support for H-bonding between the proposed oxygen atoms is provided by the Fourier map projection that shows the electron density distribution around different atoms on plane. These maps are shown in Fig. 2(a) for O_1 O_3 O_4 and in Fig. 2(b) O_1 O_2 O_4. From the figures it is clear that the electron distribution around O_1 atoms is smeared whereas it is quite symmetric for other oxygen atoms. Location of H-atom's electron distribution could provide the information regarding the nature of disorder. However, because of very small electron density distribution it could not be used quantitatively. It is not possible that the H-atoms involved in hydrogen bond are in motion either statistically (i.e. in disorder state) or dynamically.

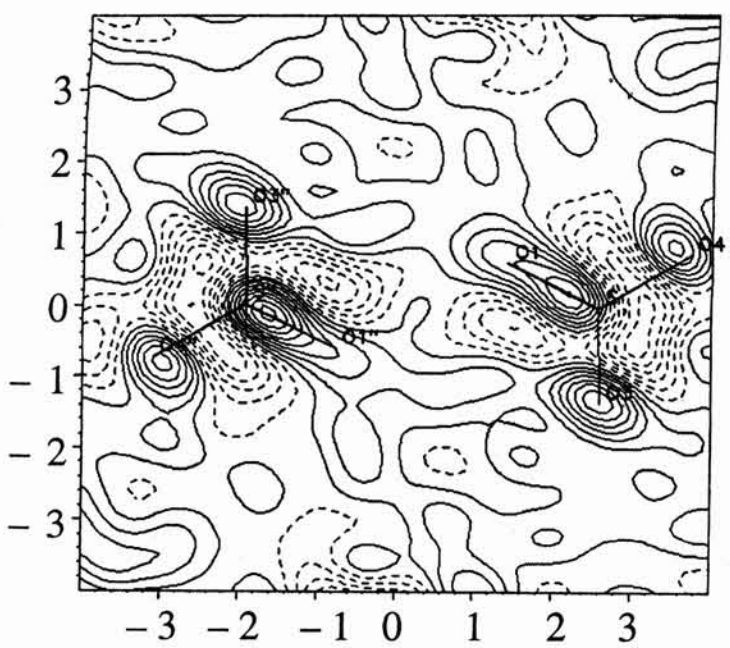

Fig. 2(a). Contour map of $SO_4 \cdot H \cdots SO_4$ dimer in $(NH_4)_3 H(SO_4)_2$ for O_1 O_3 O_4.

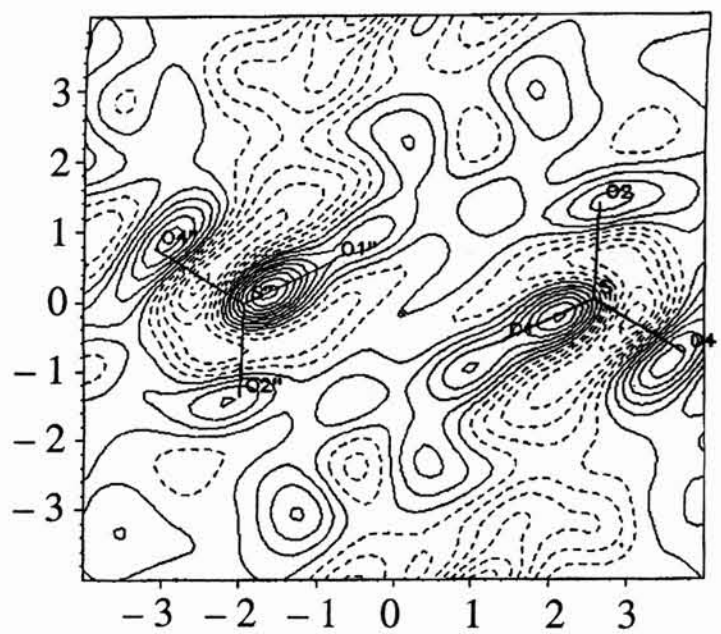

Fig. 2(b). Contour map of $SO_4 \cdot H \cdots SO_4$ dimer in $(NH_4)_3 H(SO_4)_2$ for O_1 O_2 O_4.

We also have to look after hydrogen bonding between N-O using Fourier map around N_1 and N_2. Usual Fourier synthesis does not show all the hydrogen positions. The Fourier maps through atomic position of N_1 and N_2, are shown

in Figs. 3 and 4. In the cases of N_1 and N_2, three hydrogen and two hydrogen atoms are located, respectively, by using model calculation [9]. But the interatomic distances and bond angles for the ammonium ions and those of N-H...O bonds cannot be found quantitatively in the present structure.

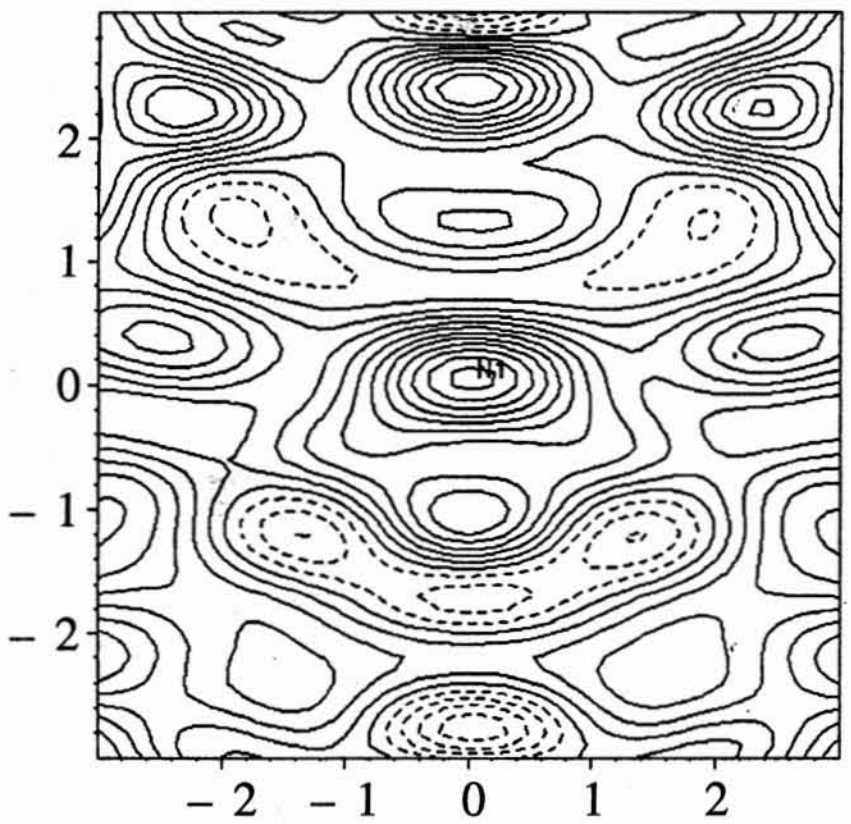

Fig. 3. Fourier map through N_1 atomic position.

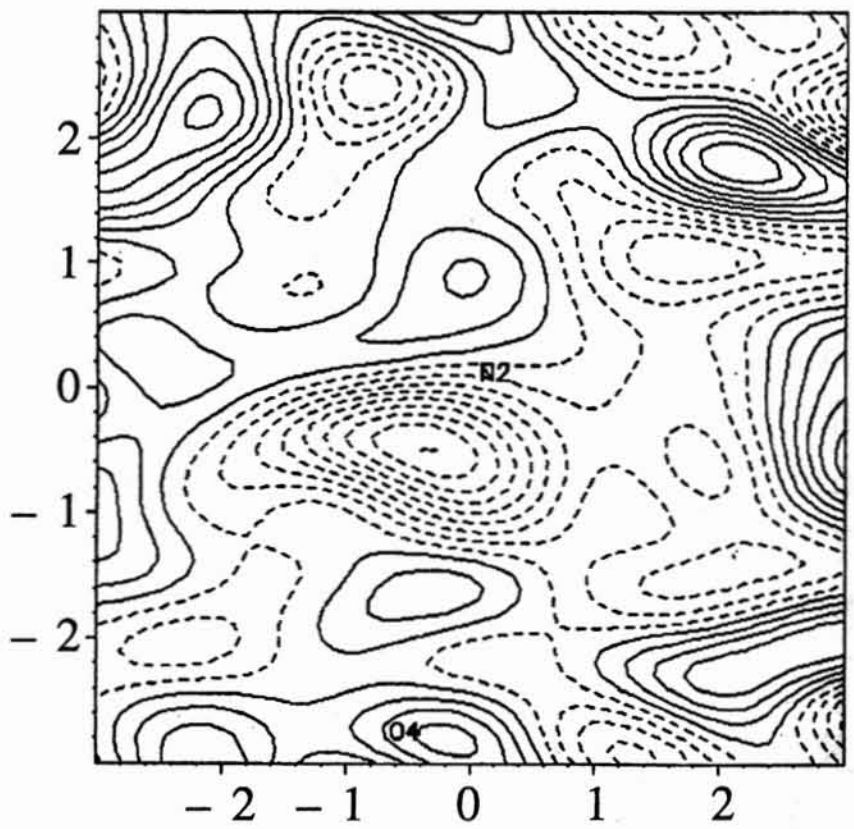

Fig. 4. Fourier map through N_2 atomic position.

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