

RESEARCH PAPERS

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Charge Density in Orthorhombic $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ at Room Temperature and 25 K

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Abstract

The charge-density distribution in the title compound nickel sulfate heptahydrate has been determined by multipole refinement against single crystal X-ray intensity data. For the refinement at 25 K hydrogen positions and displacement parameters were fixed to values determined from neutron data. The charge density based on the deformation functions of all atoms in the structure is compared with the individual densities calculated from the deformation functions of only nickel or the separate water molecules. In this way the effects of simple superposition of the individual densities have been studied. The individual deformation density around nickel is in good qualitative agreement with that expected for an approximately octahedral $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ complex in a weak ligand field. However, the maximum densities are not found precisely in the planes defined by nickel and the six water ligands, which illustrates that it is necessary to consider the crystal field due to the whole crystalline environment. The individual densities of the water molecules show clear polarization of the lone-pair densities according to the coordination of the water molecules: tetrahedral coordination leads to two resolved lone-pair peaks, whereas planar trigonal coordination leads to just one single peak. Crystal data: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $M_r = 280.87$, $P2_12_12_1$, $Z = 4$. At $T = 25$ K: $a = 6.706$ (3), $b = 11.796$ (6), $c = 11.949$ (6) Å, $V = 945$ (1) Å³, $D_x = 1.977$ Mg m⁻³. At 295 K: $a = 6.751$ (4), $b = 11.746$ (7), $c = 12.003$ (8) Å, $V = 952$ (1) Å³, $D_x = 1.959$ Mg m⁻³. X-ray study: $F(000) = 584$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.255$ mm⁻¹. At 25 K: $R(F) = 0.014$ for 10 185 reflections. At 295 K: $R(F) = 0.015$ for 5723 reflections. Neutron study at 25 K: $\lambda = 1.215$ Å, $\mu = 0.261$ mm⁻¹, $R(F) = 0.034$ for 1381 reflections.

1. Introduction

The present work is part of a series of studies on the charge and spin densities in some hydrates of 3d transition-metal salts. The charge densities of

tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and monoclinic $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ at room temperature and 25 K have been published previously (McIntyre, Ptasiewicz-Bak & Olovsson, 1990; Ptasiewicz-Bak, Olovsson & McIntyre, 1993; Kellersohn, Delaplane, Olovsson & McIntyre, 1993). The influence of the environment on the charge density of the water molecules as well as the details of the charge density of the metal ions have been studied in model deformation density maps. In the earlier studies it has been demonstrated that the true bonding deformation features are to a large extent obscured in maps based on the complete structure by superposition of the densities of adjacent atoms/molecules. The use of *partial* model deformation maps, based on individual atoms or molecules, appears to be an effective way to overcome these superposition effects and the resulting maps appear physically attractive (*cf.* Olovsson, Ptasiewicz-Bak & McIntyre, 1993). For example, the partial maps show clear polarization of the lone-pair densities of the water O atoms according to the coordination, tetrahedral or planar trigonal, of the water molecules. A significant difference was also noted between the deformation densities around Ni at room temperature and 25 K, which was tentatively attributed to changes in the relative occupations of the uppermost partially occupied energy levels of Ni. These observations are drawn from very small perturbations of the total predominantly spherical charge-density distributions. It is therefore very important to repeat these analyses in other similar structures.

Orthorhombic $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, the crystal structure of which was determined in fair detail by Beevers & Schwartz (1935), is a good example for comparison (note that the diagrams of Figs. 4 and 5 of this reference, describing the bond structures in $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, are interchanged). It consists of tetrahedral SO_4 and octahedral $\text{Ni}(\text{H}_2\text{O})_6$ groups, as in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, but with one extra water molecule, and the water molecules exhibit both tetrahedral and trigonal coordination. All six water molecules around nickel are crystallographically unique, which should provide a good internal comparison of the polarization according to coordination.

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Table 1. *Experimental details*

	295 K X-ray	25 K neutron	25 K X-ray
Crystal data			
Chemical formula	NiSO ₄ ·7H ₂ O	NiSO ₄ ·7H ₂ O	NiSO ₄ ·7H ₂ O
Chemical formula weight	280.87	280.87	280.87
Cell setting	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	6.751 (4)	6.706 (3)*	6.706 (3)
<i>b</i> (Å)	11.746 (7)	11.796 (6)	11.796 (6)
<i>c</i> (Å)	12.003 (8)	11.949 (6)	11.949 (6)
<i>V</i> (Å ³)	952 (1)	945 (1)	945 (1)
<i>Z</i>	4	4	4
<i>D_x</i> (Mg m ⁻³)	1.959	1.977	1.977
Radiation type	Mo <i>K</i> α	Neutron	Mo <i>K</i> α
Wavelength (Å)	0.71069	1.215	0.71069
No. of reflections for cell parameters	20	—	20
θ range (°)	20–40	—	20–40
μ (mm ⁻¹)	2.255	0.261	2.255
Temperature (K)	295	25	25
Crystal form	Rectangular prism	Rectangular prism	Rectangular prism
Crystal size (mm)	0.48 × 0.40 × 0.30	7.0 × 2.3 × 1.6	0.24 × 0.21 × 0.21
Crystal colour	Green	Green	Green
Data collection			
Diffractometer	Stoe four-circle	Huber–Aracor four circle	Huber–Aracor 400 mm diameter four circle
Data collection method	ω -2 θ scans	ω -2 θ scans	ω -2 θ scans
Absorption correction	Gaussian (Coppens, Leiserowitz & Rabinovitch, 1965)	Gaussian integration using $\mu = 0.261 \text{ mm}^{-1}$	Gaussian (Coppens, Leiserowitz & Rabinovitch, 1965)
<i>T</i> _{min}	0.43	0.53	0.57
<i>T</i> _{max}	0.54	0.68	0.67
No. of measured reflections	7733	1849	10 988
No. of independent reflections	6240	1381	10 415
No. of observed reflections	5723	1849	10 185
Criterion for observed reflections	$F_o^2 > 5\sigma(F_o^2)$	None	$F_o^2 > 3\sigma(F_o^2)$
<i>R</i> _{int}	0.020	0.042	0.019
θ_{max} (°)	45	53.3	50
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 13 -23 → <i>k</i> → 23 -16 → <i>l</i> → 23	-5 → <i>h</i> → 8 -6 → <i>k</i> → 15 -15 → <i>l</i> → 15	0 → <i>h</i> → 15 0 → <i>k</i> → 26 -25 → <i>l</i> → 26
No. of standard reflections	5	1	6
Frequency of standard reflections	240 min	Every 33 reflections	240 min
Intensity decay (%)	None	None	None
Refinement			
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
<i>R</i> (<i>F</i>)	0.0137	0.034	0.0149
<i>wR</i> (<i>F</i> ²)	0.0327	0.046	0.0338
<i>S</i>	2.162	1.68	1.458
No. of reflections used in refinement	5723	1381	10 185
No. of parameters used	297	245	297
H-atom treatment	H atoms: see text, O—H 0.97 Å	Refined	H atoms placed at positions found by neutron diffraction
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + k^2 F_o^4]$	$w = 1/[\sigma^2(F_o^2) + k^2 F_o^4]$	$w = 1/[\sigma^2(F_o^2) + k^2 F_o^4]$
(Δ/σ) _{max}	0.008	0.25 (extinction parameter)	0.001
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.25	—	0.15
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-0.25	—	-0.15
Extinction method	Gaussian type I isotropic (Becker & Coppens, 1974, 1975)	Lorentzian type I isotropic (Becker & Coppens, 1974, 1975)	Gaussian type I isotropic (Becker & Coppens, 1974, 1975)
Extinction coefficient	21 610	$\gamma = 0.80$	5552
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV) for Ni, S and O, and Stewart, Davidson & Simpson (1965) for H	Sears (1992)	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV) for Ni, S and O, and Stewart, Davidson & Simpson (1965) for H

* From the 25 K X-ray data.

2. Experimental

Slow evaporation at 295 K of a concentrated solution of nickel sulfate produced deep-green semi-translucent rectangular crystals which exhibited the forms {011} and {111}.

2.1. X-ray data

Intensity data were collected at room temperature and at 25 K; most experimental details are given in Table 1. To avoid dehydration the crystal used in the room-temperature collection was mounted inside a thin-

walled glass capillary. Graphite (002) monochromatized Mo $K\alpha$ radiation was used in both measurements. All equivalent reflections to $\sin \theta/\lambda = 0.364 \text{ \AA}^{-1}$ and an almost complete set of reflections for all $\pm h, \pm k$ and $+l$ to $\sin \theta/\lambda = 0.995 \text{ \AA}^{-1}$ were measured at room temperature; at 25 K all equivalent reflections were measured to $\sin \theta/\lambda = 0.364 \text{ \AA}^{-1}$ and a set for $\pm h, +k, +l$ to $\sin \theta/\lambda = 1.077 \text{ \AA}^{-1}$. Average instability constants were 0.0065 and 0.0058, respectively. Background corrections following Lehmann & Larsen (1974) and Lorentz and polarization corrections were applied.

2.2. Neutron data

The neutron diffraction data were measured at the R2 reactor in Studsvik, Sweden, in a beam of wavelength 1.215 \AA obtained by reflection from a Cu(220) double monochromator, see Table 1. The long axis of the crystal was mounted parallel to the diffractometer φ axis. All unique reflections with h, k and $l > 0$ to $\sin \theta/\lambda = 0.66 \text{ \AA}^{-1}$ were measured, as well as most equivalent reflections with h and $k > 0$ and $l < 0$ in the range $0.53 < \sin \theta/\lambda < 0.66 \text{ \AA}^{-1}$; 10–15 min per reflection. Background corrections following Lehmann & Larsen (1974) and Lorentz corrections were applied.

Collection of data at room temperature from this crystal was then attempted, but was soon terminated due to the gradual dehydration of the crystal in the dry atmosphere in the reactor experimental hall.

All data reduction programs and the full-matrix program *UPALS* used for structure refinement and fitting of the charge deformation have been described by Lundgren (1982).

3. Refinements

The atomic positions of the heavy atoms from the previous X-ray study (Beevers & Schwartz, 1935) were used as starting values in the conventional refinement of our room-temperature X-ray data and the hydrogen-bonding scheme proposed earlier was confirmed. The coordinates derived were used as starting values in all later refinements at room temperature and 25 K. In all refinements the quantity minimized was $\sum w(F_o^2 - F_c^2)^2$, using weights according to $w^{-1} = \sigma^2(F_o^2) + k^2 F_o^4$, where σ^2 was derived from Poisson counting statistics and k was fixed at 0.01; the constant k was determined empirically from weighting analyses.

3.1. Neutron data

Refinement details are given in Table 1. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2(b).

3.2. X-ray data

Two sets of refinements were carried out for both the room temperature and 25 K data: (i) a conventional refinement with the assumption of spherical atomic

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3) \sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
295 K X-ray				
Ni	0.04106 (2)	0.42089 (1)	0.10442 (1)	0.01753 (5)
S	0.49094 (2)	0.72630 (2)	0.18354 (2)	0.01873 (9)
O1	0.42704 (17)	0.68381 (12)	0.07465 (9)	0.0371 (5)
O2	0.48169 (14)	0.85142 (7)	0.18668 (10)	0.0309 (4)
O3	0.69542 (13)	0.68889 (9)	0.20501 (10)	0.0322 (4)
O4	0.36068 (14)	0.67853 (8)	0.27191 (8)	0.0274 (3)
O5	0.00529 (8)	0.26070 (6)	0.16624 (10)	0.0270 (4)
O6	0.18986 (16)	0.46923 (5)	0.24842 (5)	0.0233 (4)
O7	-0.22480 (14)	0.46753 (6)	0.16931 (8)	0.0296 (4)
O8	0.07373 (10)	0.58217 (9)	0.04556 (8)	0.0331 (4)
O9	-0.10690 (9)	0.37229 (7)	-0.03912 (10)	0.0261 (3)
O10	0.29961 (15)	0.36550 (7)	0.03700 (10)	0.0342 (5)
O11	-0.06940 (15)	0.48952 (13)	0.43590 (6)	0.0336 (5)
25 K neutron				
Ni	0.04120 (12)	0.41850 (7)	0.10334 (6)	0.0047 (2)
S	0.4927 (4)	0.7226 (2)	0.1809 (2)	0.0046 (7)
O1	0.4282 (2)	0.6792 (1)	0.0720 (1)	0.0069 (3)
O2	0.4813 (2)	0.8485 (1)	0.1819 (1)	0.0071 (3)
O3	0.6986 (2)	0.6867 (1)	0.2040 (1)	0.0068 (3)
O4	0.3615 (2)	0.6773 (1)	0.2709 (1)	0.0067 (3)
O5	0.0043 (2)	0.2587 (1)	0.1652 (1)	0.0070 (4)
O6	0.1898 (2)	0.4680 (1)	0.2492 (1)	0.0067 (3)
O7	-0.2295 (2)	0.4646 (1)	0.1675 (1)	0.0079 (4)
O8	0.0711 (2)	0.5785 (1)	0.0435 (1)	0.0081 (4)
O9	-0.1045 (2)	0.3701 (1)	-0.0418 (1)	0.0069 (4)
O10	0.3051 (2)	0.3635 (1)	0.0390 (1)	0.0082 (4)
O11	-0.0711 (2)	0.4925 (1)	0.4333 (1)	0.0079 (4)
H51	0.1073 (5)	0.2327 (2)	0.2178 (2)	0.0209 (8)
H52	-0.1258 (5)	0.2354 (3)	0.1933 (2)	0.0206 (8)
H61	0.3017 (4)	0.4180 (2)	0.2701 (2)	0.0196 (7)
H62	0.2476 (4)	0.5449 (2)	0.2492 (2)	0.0202 (8)
H71	-0.3073 (5)	0.4215 (3)	0.2208 (2)	0.0230 (8)
H72	-0.2536 (5)	0.5451 (2)	0.1803 (2)	0.0205 (8)
H81	0.1954 (5)	0.6219 (2)	0.0531 (2)	0.0216 (8)
H82	0.0143 (5)	0.6037 (3)	-0.0263 (3)	0.0252 (8)
H91	-0.0222 (5)	0.3634 (2)	-0.1087 (2)	0.0217 (7)
H92	-0.2197 (4)	0.4185 (3)	-0.0593 (2)	0.0199 (7)
H101	0.3349 (5)	0.2840 (3)	0.0291 (3)	0.0217 (7)
H102	0.4032 (5)	0.4090 (3)	0.0001 (2)	0.0215 (7)
H111	-0.0544 (5)	0.4274 (3)	0.4815 (2)	0.0245 (8)
H112	-0.0010 (5)	0.4746 (3)	0.3650 (2)	0.0248 (8)
25 K X-ray				
Ni	0.041148 (8)	0.418464 (5)	0.103336 (4)	0.00330 (2)
S	0.493171 (14)	0.723098 (9)	0.180883 (9)	0.00365 (3)
O1	0.42800 (5)	0.67914 (3)	0.07186 (3)	0.0068 (1)
O2	0.48151 (5)	0.84873 (3)	0.18183 (3)	0.0061 (1)
O3	0.69950 (5)	0.68665 (3)	0.20373 (3)	0.0065 (1)
O4	0.36109 (5)	0.67726 (3)	0.27108 (3)	0.0061 (1)
O5	0.00398 (5)	0.25867 (3)	0.16514 (3)	0.0065 (1)
O6	0.18979 (6)	0.46803 (3)	0.24910 (3)	0.0061 (1)
O7	-0.22951 (5)	0.46441 (3)	0.16713 (3)	0.0069 (1)
O8	0.07134 (5)	0.57943 (3)	0.04371 (3)	0.0071 (1)
O9	-0.10487 (5)	0.36998 (3)	-0.04192 (3)	0.0062 (1)
O10	0.30489 (6)	0.36346 (3)	0.03906 (3)	0.0079 (1)
O11	-0.07086 (5)	0.49267 (4)	0.43325 (3)	0.0077 (1)

scattering factors and (ii) deformation refinements in which the experimental electron distribution was fitted to multipole deformation functions. Most refinement details are given in Table 1.

For the room-temperature data the hydrogen positional and isotropic displacement parameters in the deformation refinements (ii) were fixed to the values derived from the conventional X-ray refinement, but with the positions shifted out to 0.97 \AA from the

appropriate water O atom. The positional parameters thus derived, together with the standard deviations obtained in the conventional refinement, are given in Table 2(a) and were used for distance and angle calculations involving H atoms at room temperature. The crystal used for the room-temperature data collection was rather large and mounted in a thin-walled glass capillary; due to the resulting lower accuracy only the 5723 reflections with $F_o^2 > 5\sigma(F_o^2)$ were used in the final conventional and deformation refinements. If reflections with $F_o^2 > 3\sigma(F_o^2)$ were used instead, the *R* values increased significantly.

For the 25 K data the positional parameters for hydrogen were fixed to the neutron values. The refined coordinates for atoms other than H agreed very well with the neutron coordinates, but the displacement parameters were systematically higher in the neutron case. The average ratio $\beta(\text{X-ray})/\beta(\text{neutron})$ for atoms other than H was 0.872, with very little individual variation. In the final X-ray refinements the anisotropic displacement parameters for hydrogen were therefore fixed to the neutron values multiplied by 0.872. Only the 10 185 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the final refinements.

3.2.1. Conventional refinement. The following parameters were refined: scale factor, mosaic width, positional and anisotropic displacement parameters of all atoms other than the H atoms; for the room-temperature data the positional and isotropic displacement parameters for hydrogen were refined, for the 25 K data the treatment of hydrogen has been described above.

3.2.2. Deformation refinement. To minimize the effects of experimental noise and the phase uncertainty in this non-centrosymmetric structure, the experimental electron deformation density was modelled by multipole refinement by least-squares, using deformation functions proposed by Hirshfeld (1971) with modifications by Harel & Hirshfeld (1975) and Hirshfeld (1977). The charge density was modelled by an expansion of up

to 35 terms centred on each atom. Details of the procedure were given in a previous paper (McIntyre, Ptasiwicz-Bak & Olovsson, 1990).

A series of deformation refinements were performed where initially imposed symmetry constraints were successively relaxed and the level of multipoles *n* increased. Strong correlation effects prohibited simultaneous refinement of the γ parameters, which determine the breadth of the radial functions, together with the other deformation functions. Therefore, their values were chosen on the basis of an analysis of the results of refinements with fixed γ parameters in the range $\gamma = 2.0\text{--}7.0$ for Ni and $\gamma = 2.0\text{--}5.0$ for S, O and H atoms. Gaussian radial functions were used, since for exponential radial functions the refinements diverged. Modifying the values of γ within reasonable limits had very little effect on the total deformation density maps, but γ values outside these limits changed the maps drastically and were not chemically reasonable.

In the final sets at both temperatures the following parameters were refined (γ fixed to 4.0 for all atoms). (i) Ni and S: *x, y, z, β_{ij} ; $n \leq 4$* ; 18 deformation parameters per atom. Twofold symmetry imposed. (ii) O atoms in the sulfate ion: *x, y, z, β_{ij} ; $n \leq 2$* ; 10 deformation parameters per atom. No symmetry restrictions and all oxygens treated independently. (iii) O atoms in the water molecules: *x, y, z, β_{ij} ; $n \leq 4$* ; 14 deformation parameters per atom; *mm2* symmetry imposed, all oxygens treated independently. (iv) H: *n ≤ 2* ; 4 deformation parameters. Cylindrical symmetry imposed, all hydrogens assumed to be equivalent. The positional and displacement parameters were fixed as described above. The arbitrariness in the refined sums of the odd-order multipole terms – a potential problem in all non-centrosymmetric structures (Terpstra, Craven & Stewart, 1993) – was avoided by the chemically reasonable assumption that the bonding deformations of all H atoms are equivalent.

In total, 178 deformation parameters were refined. In addition, the scale factor and an isotropic extinction

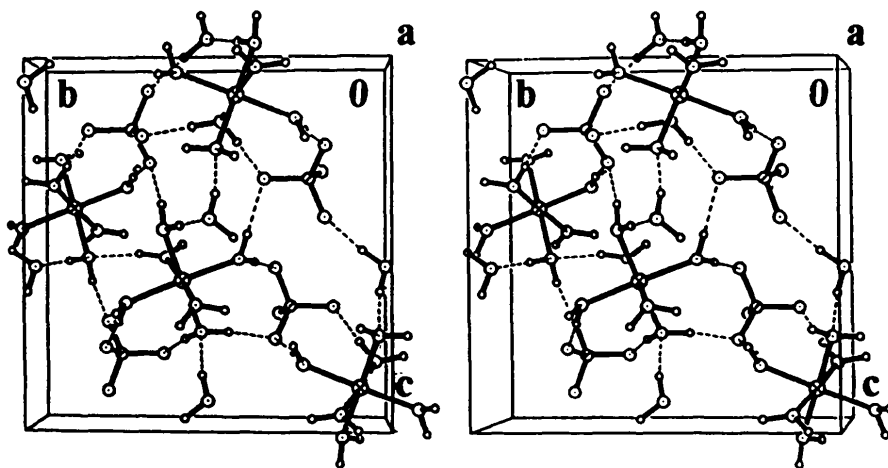


Fig. 1. Stereoscopic picture of the crystal structure of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$. The *a* axis is directed towards the reader.

parameter were refined as in the conventional refinements.

If no symmetry restrictions were imposed on nickel the fit did not improve and the features in the maps were approximately the same. If the symmetry restrictions on the water oxygens were removed the features in the lone-pair regions were similar but not quite symmetrical; however, two maxima were still present when the restrictions were removed.

Local axes for the multipole functions were assumed. The possible dependence of the results on this assumption was checked by inspecting the goodness-of-fit and deformation density maps in three independent refinements at both temperatures. The local axes for the multipole functions for nickel were then assumed to be: to oxygen O5 in the first refinement, to the nearest Ni atom in the second and to the nearest S atom in the third. The goodness-of-fit as well as the density features in the maps were found to be quite independent of the local coordination system assumed.

The agreement factors from the different refinements are given in Table 1. The positional and equivalent isotropic displacement parameters from the final model refinement are given in Table 2.*

4. Results and discussion

The crystal structure is illustrated in Fig. 1. Selected distances and angles are listed in Table 3. All seven water molecules are crystallographically independent. The nickel ion is surrounded by six water molecules in a close-to-octahedral arrangement (Fig. 2); Ni—O distances range from 2.034 to 2.090 Å, O—Ni—O angles from 87.0 to 94.5° (from the X-ray study at 25 K). The average Ni—O distance, 2.053 Å, is in close agreement with the average value, 2.051 Å, in NiSO₄·6H₂O at 25 K (Ptasiewicz-Bak, Olovsson & McIntyre, 1993). The geometry of the coordination of these water molecules to nickel is shown in Fig. 3: the coordination to water(5) (*i.e.* water with O5), water(6) and (9) is close to tetrahedral (in one of the lone-pair directions), to water(10) almost trigonal planar, and in-between to water(7) and (8). Most of these water molecules donate hydrogen bonds to sulfate oxygens. The non-coordinated water (11) is hydrogen-bonded to one sulfate oxygen and to three of the water molecules. All hydrogen bonds are of medium strength; O—O distances range from 2.67 to 2.89 Å, O—H...O angles (neutron) from 159 to 179°. The average O—H distance in the water molecules from the neutron study at 25 K is 0.974 (not corrected for riding motion), the average H—O—H angle is 107.2°. In NiSO₄·6H₂O at 25 K the average O—H distance was

observed to be 0.975 Å. These values are close to the average distance $r_g = 0.974$ Å in the vibrational ground state of the free water molecule (Kuchitsu & Bartell, 1962).

The geometry of the sulfate ion is almost ideally tetrahedral. The average S—O distance in the sulfate ion from the X-ray study at 25 K is 1.480 Å and the average O—S—O angle 109.9°. At 295 K the corre-

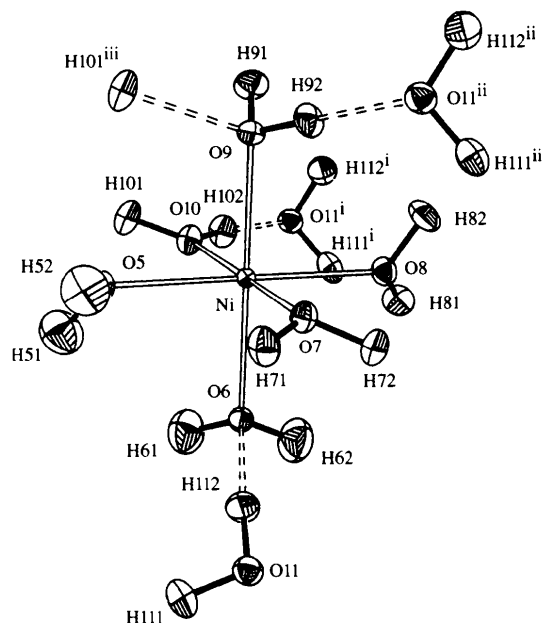
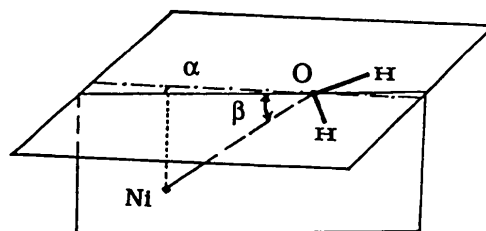


Fig. 2. The approximately octahedral coordination of the six water molecules around nickel. The seventh water molecule, not coordinated to Ni, is also shown. The thermal ellipsoids correspond to 50% probability. Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (ii) $-\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, -z$.



plane	β [°]	α [°]
(O5, H51, H52)	37.1	0.0
(O6, H61, H62)	45.9	2.8
(O7, H71, H72)	16.3	4.6
(O8, H81, H82)	22.5	4.6
(O9, H91, H92)	44.7	3.7
(O10, H101, H102)	11.6	3.4

Fig. 3. The geometry of the coordination of the water molecules to nickel.

* Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: AB0357). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected bond lengths (Å) and angles (°) for NiSO₄·7H₂O

Standard deviations are given in parentheses; atomic positions, except for hydrogen, from the X-ray deformation refinements. Hydrogen positions and standard deviations: at 25 K from neutron data results, at 295 K, see text.

Bond

(a) Covalent bonds

	at 295 K	at 25 K		at 295 K	at 25 K
Ni—O5	2.037 (1)	2.040 (1)	O5—Ni—O6	90.38 (3)	90.87 (2)
Ni—O6	2.078 (1)	2.090 (1)	O5—Ni—O7	90.27 (3)	90.09 (1)
Ni—O7	2.032 (1)	2.042 (1)	O5—Ni—O8	178.79 (4)	178.45 (1)
Ni—O8	2.034 (2)	2.038 (1)	O5—Ni—O9	89.50 (4)	89.45 (2)
Ni—O9	2.072 (1)	2.073 (1)	O5—Ni—O10	87.20 (3)	87.03 (1)
Ni—O10	2.031 (1)	2.034 (1)	O6—Ni—O7	91.98 (4)	92.21 (2)
			O6—Ni—O8	88.97 (3)	89.04 (1)
			O6—Ni—O9	179.85 (3)	179.59 (1)
			O6—Ni—O10	90.21 (4)	89.38 (2)
			O7—Ni—O8	88.73 (3)	88.37 (1)
			O7—Ni—O9	88.12 (4)	88.04 (2)
			O7—Ni—O10	176.67 (3)	176.73 (1)
			O8—Ni—O9	91.15 (4)	90.65 (2)
			O8—Ni—O10	93.83 (3)	94.52 (1)
			O9—Ni—O10	89.69 (4)	90.38 (2)
S—O1	1.464 (1)	1.469 (1)	O1—S—O2	110.54 (7)	110.10 (2)
S—O2	1.471 (1)	1.484 (1)	O1—S—O3	109.33 (7)	109.91 (2)
S—O3	1.471 (1)	1.474 (1)	O1—S—O4	109.50 (6)	109.58 (2)
S—O4	1.488 (1)	1.496 (1)	O2—S—O3	109.49 (6)	109.83 (2)

(b) Water molecules

O5—H51	0.97 (2)	0.985 (3)	H51—O5—H52	111.5 (9)	108.7 (2)
O5—H52	0.97 (2)	0.973 (3)			
O6—H61	0.97 (1)	0.987 (3)	H61—O6—H62	103.5 (8)	104.4 (2)
O6—H62	0.97 (1)	0.986 (3)			
O7—H71	0.97 (2)	0.969 (3)	H71—O7—H72	108.1 (9)	108.2 (2)
O7—H72	0.97 (2)	0.979 (3)			
O8—H81	0.97 (2)	0.978 (3)	H81—O8—H82	107.4 (9)	106.5 (3)
O8—H82	0.97 (2)	0.964 (3)			
O9—H91	0.97 (2)	0.975 (3)	H91—O9—H92	109.8 (9)	108.6 (2)
O9—H92	0.97 (2)	0.982 (3)			
O10—H101	0.97 (2)	0.966 (3)	H101—O10—H102	114.3 (9)	109.7 (3)
O10—H102	0.97 (1)	0.970 (3)			
O11—H111	0.97 (2)	0.968 (3)	H111—O11—H112	103.8 (8)	105.9 (3)
O11—H112	0.97 (2)	0.964 (3)			

(c) Hydrogen bonds at 295 K

O5...O3	2.680 (2)	H51...O3	1.71 (2)	O5—H51...O3	175 (2)
O5...O4	2.755 (2)	H52...O4	1.79 (2)	O5—H52...O4	170 (2)
O6...O2	2.727 (2)	H61...O2	1.77 (2)	O6—H61...O2	168 (2)
O6...O4	2.730 (2)	H62...O4	1.76 (2)	O6—H62...O4	172 (2)
[O11...O6	2.861 (2)	H112...O6	1.92 (2)	O11—H112...O6	162 (1)]
O7...O2	2.803 (2)	H71...O2	1.83 (2)	O7—H71...O2	175 (1)
O7...O3	2.690 (2)	H72...O3	1.72 (2)	O7—H72...O3	174 (1)
O8...O1	2.690 (2)	H81...O1	1.72 (2)	O8—H81...O1	173 (2)
O8...O2	2.961 (2)	H82...O2	2.05 (1)	O8—H82...O2	154 (2)
O9...O4	2.875 (2)	H91...O4	1.92 (2)	O9—H91...O4	169 (2)
O9...O11	2.739 (2)	H92...O11	1.77 (2)	O9—H92...O11	171 (2)
[O10...O9	2.864 (2)	H101...O9	1.91 (2)	O10—H101...O9	165 (2)]
O10...O9	2.864 (2)	H101...O9	1.91 (2)	O10—H101...O9	165 (2)
O10...O11	2.773 (2)	H102...O11	1.80 (1)	O10—H102...O11	176 (2)
O11...O1	2.801 (2)	H111...O1	1.87 (2)	O11—H111...O1	160 (2)
O11...O6	2.861 (2)	H112...O6	1.92 (2)	O11—H112...O6	162 (1)
[O9...O11	2.739 (2)	H92...O11	1.77 (2)	O9—H92...O11	171 (2)]
[O10...O11	2.773 (2)	H102...O11	1.80 (1)	O10—H102...O11	176 (2)]

(d) Hydrogen bonds at 25 K

O5...O3	2.670 (1)	H51...O3	1.688 (3)	O5—H51...O3	173.9 (3)
O5...O4	2.738 (1)	H52...O4	1.772 (3)	O5—H52...O4	171.4 (2)
O6...O2	2.742 (1)	H61...O2	1.764 (3)	O6—H61...O2	170.6 (2)
O6...O4	2.735 (1)	H62...O4	1.756 (3)	O6—H62...O4	171.1 (2)
[O11...O6	2.825 (1)	H112...O6	1.887 (3)	O11—H112...O6	163.6 (2)]
O7...O2	2.824 (1)	H71...O2	1.859 (3)	O7—H71...O2	173.4 (2)

Table 3 (*cont.*)(d) Hydrogen bonds at 25 K (*cont.*)

O7...O3	2.700 (1)	H72...O3	1.721 (3)	O7—H72...O3	178.9 (2)
O8...O1	2.686 (1)	H81...O1	1.714 (3)	O8—H81...O1	172.3 (2)
O8...O2	2.888 (1)	H82...O2	1.952 (3)	O8—H82...O2	163.0 (2)
O9...O4	2.824 (1)	H91...O4	1.860 (3)	O9—H91...O4	169.4 (2)
O9...O11	2.728 (1)	H92...O11	1.754 (3)	O9—H92...O11	170.7 (2)
[O10...O9	2.820 (1)	H101...O9	1.867 (3)	O10—H101...O9	168.3 (2)]
O10...O9	2.820 (1)	H101...O9	1.867 (3)	O10—H101...O9	168.3 (2)
O10...O11	2.767 (1)	H102...O11	1.801 (3)	O10—H102...O11	173.6 (2)
O11...O1	2.787 (1)	H111...O1	1.861 (3)	O11—H111...O1	159.1 (2)
O11...O6	2.825 (1)	H112...O6	1.887 (3)	O11—H112...O6	163.6 (2)
[O9...O11	2.728 (1)	H91...O11	1.754 (3)	O9—H92...O11	170.7 (2)]
[O10...O11	2.767 (1)	H102...O11	1.801 (3)	O10—H102...O11	173.6 (2)]

sponding X-ray values are 1.474 Å and 109.7°. This foreshortening of the S—O distance at room temperature compared with 25 K, 0.006 Å, is most probably an artifact of larger anisotropic displacements of the O atoms at room temperature. Correction for riding motion gives an average value of 1.484 Å at 25 K and 1.487 Å at room temperature. The corresponding average S—O distances in NiSO₄·6H₂O, 1.481 Å at 25 K and 1.490 Å at room temperature, are in close agreement with the present values.

4.1. Deformation charge densities

Some general arguments for the use of deformation model maps instead of $X - N$ maps were given in a previous paper (McIntyre, Ptasiwicz-Bak & Olovsson, 1990). This approach also makes it possible to calculate partial deformation maps to eliminate effects due to superposition of the deformation functions of neighbouring atoms (*cf.* Olovsson, Ptasiwicz-Bak & McIntyre, 1993). In the maps the three atoms defining each plane are written without parentheses. For orientation purposes other atoms close to these planes and the relevant H atoms are indicated within parentheses. In an attempt to distinguish the characteristic features of the nickel ion and the water molecules, the maps calculated from only the deformation functions of each of these constituents are also plotted separately. All maps shown are static multipole deformation maps; the corresponding dynamic maps are very similar. Only a few of all the maps calculated are illustrated here.

4.1.1. *The nickel ion.* The total and partial deformation densities at 25 K and room temperature in the plane defined by Ni, O5 and O6 are shown in Figs. 4(a) and (a'). For unknown reasons the superposition effects are less pronounced in the present case than in NiSO₄·6H₂O. These maps may be taken as typical representatives of the characteristic features in the other planes defined by nickel and the ligands in the coordination octahedron. In these other planes only partial deformation densities are shown in Figs. 4(b) and (c).

Qualitatively, the features in the maps – deficiency in the ligand directions compared with the diagonal

Table 4. *The geometry (Å, °) of the nearest nickel neighbours of the nickel ion in the NiSO₄·7H₂O structure at 295 and 25 K*

	295 K	25 K
Ni—Ni ⁱ	5.814 (2)	5.757 (2)
Ni—Ni ⁱⁱ	5.814 (2)	5.757 (2)
Ni—Ni ⁱⁱⁱ	6.751 (3)	6.706 (3)
Ni—Ni ^{iv}	6.751 (3)	6.706 (3)
Ni—Ni ^v	6.887 (3)	6.873 (3)
Ni—Ni ^{vi}	6.887 (3)	6.873 (3)
Ni—Ni ^{vii}	6.856 (3)	6.883 (3)
Ni—Ni ^{viii}	6.856 (3)	6.883 (3)
Ni—Ni ^{ix}	7.411 (3)	7.392 (3)
Ni—Ni ^x	7.411 (3)	7.392 (3)
Ni ⁱⁱⁱ —Ni—Ni ^v	114.18 (2)	114.05 (1)
Ni ⁱⁱⁱ —Ni—Ni ^{vii}	85.36 (1)	85.40 (1)
Ni ^v —Ni—Ni ^{vii}	104.25 (3)	103.62 (3)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (iii) $x - 1, y, z$; (iv) $1 + x, y, z$; (v) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (vi) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (vii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (viii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (ix) $-\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (x) $-\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$.

directions – are those expected for a Ni²⁺ ion in a weak, approximately octahedral crystal field: a $d_e^6 d_\gamma^2$ electron configuration where the diagonally directed d_e orbitals (d_{x^2} , d_{y^2} and d_{z^2}) are all completely full, whereas the two d_γ orbitals share two electrons. The distances and angles in the coordination octahedron at 25 and 295 K are not significantly different (Table 3). The maximum difference is observed for Ni—O6: 2.090 (1) Å at 25 K and 2.078 (1) Å at 295 K. The differences in the electron densities around nickel at 25 and 295 K are obviously not due to changes in the nearest environment.

A very extensive search in other planes around nickel have shown that the maximum features are actually not in the planes just mentioned, but in certain planes defined by nickel and the nearest nickel neighbours in the geometry shown in Fig. 6 and Table 4. This is illustrated by the partial maps in three planes through nickel in Figs. 5(a)–(c). The maximum electron density is observed along the Ni—Ni^{vii} direction at 25 K and along the Ni—Ni^v direction at 295 K, as shown in Fig. 5(a). There is a small but significant change in the

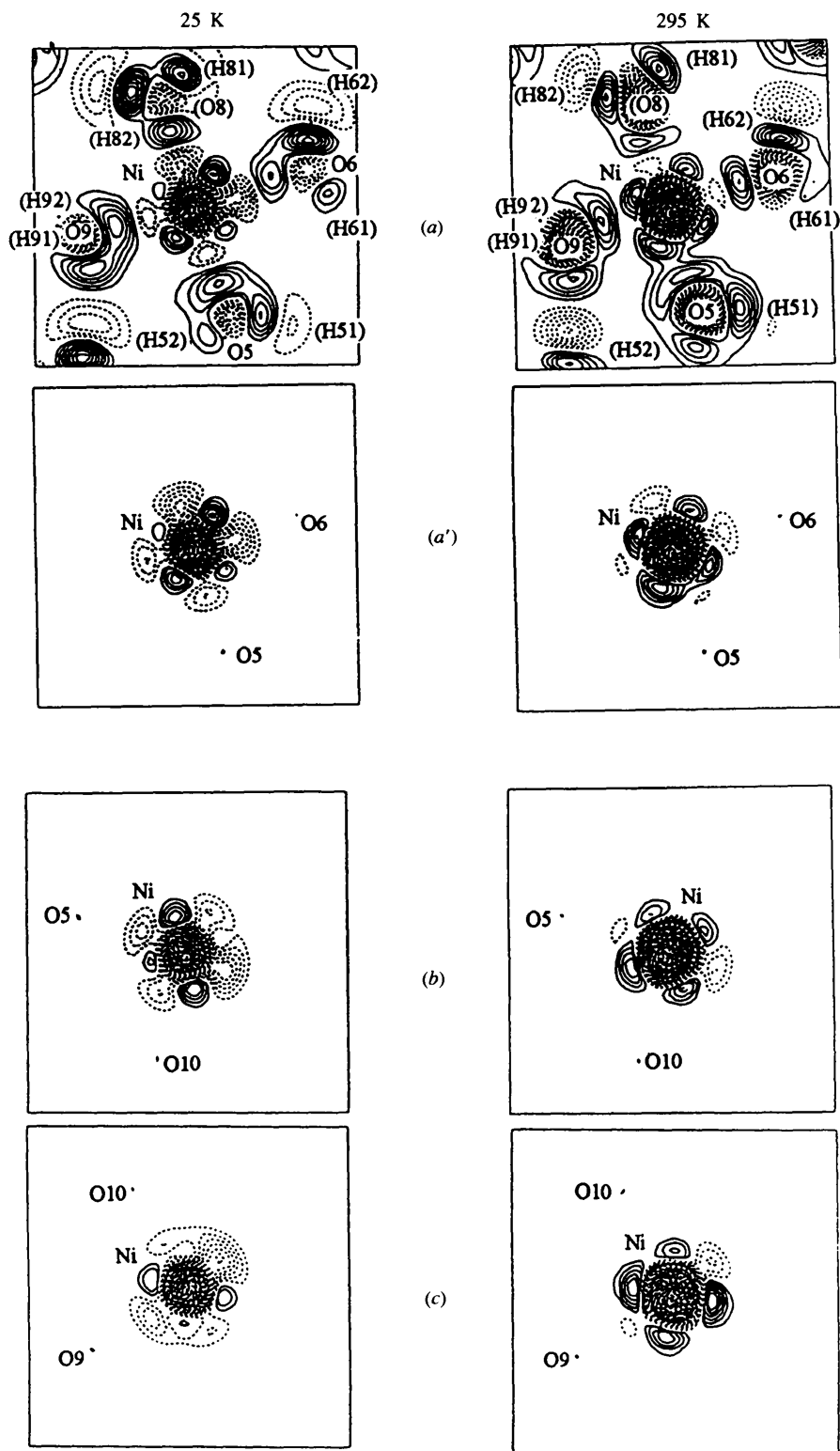


Fig. 4. Deformation densities at 25 and 295 K. (a) and (a') in the plane defined by Ni, O5 and O6; (b) by Ni, O5 and O10; (c) by Ni, O9 and O10. (a) All deformation functions included (total deformation maps). (a'), (b) and (c) only deformation functions centred on Ni included (partial deformation maps). Contours in Figs. 5–8 are drawn at intervals of $0.05 \text{ e} \text{ \AA}^{-3}$. Negative contours are dashed; the zero contour is omitted.

distances: Ni—Ni^{vii} is longer at 25 K, whereas Ni—Ni^v is longer at 295 K. The distances Ni—Ni^v and Ni—Ni^{vii} are 6.873 (3) and 6.883 (3) Å at 25 K and 6.887 (3) and 6.856 (3) Å at 295 K, respectively (Table 4). Other Ni—Ni pairs do not show similar inversion in the distances with temperature. It seems quite possible that small differences in the structural arrangement between 25 and 295 K may cause such a change in direction of the maximum of the electron density. However, we

do not want to draw any definite conclusions from the present study as the relative experimental uncertainty must also be considered: The room-temperature maps are less reliable than the 25 K maps, because the thermal parameters are larger in the room-temperature study (and significant anharmonic contributions are likely), a larger crystal was used and no neutron data were available.

A corresponding extensive search of the features in different planes around nickel in other compounds

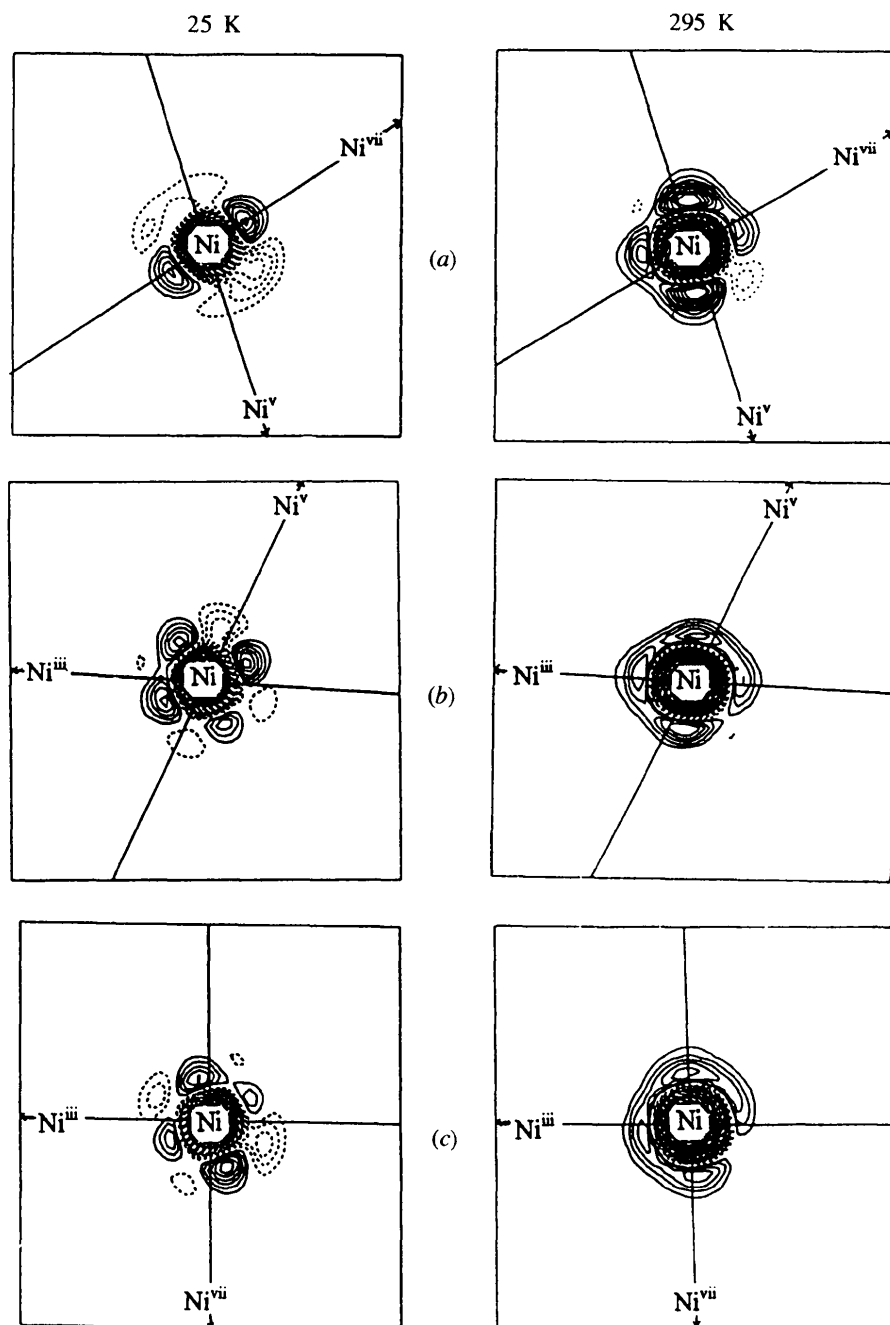


Fig. 5. Partial deformation maps in three different planes through nickel, which do not involve the water ligands in the coordination octahedron, at 25 and 295 K. (a) Plane perpendicular to the Ni—Niⁱⁱⁱ line (Ni^v and Ni^{vii} are close to this plane); (b) plane perpendicular to the Ni—Ni^{vii} line; (c) plane perpendicular to the Ni—Ni^v line. Niⁱⁱⁱ, Ni^v and Ni^{vii} denote the equivalent positions described in Table 4 and illustrated in Fig. 6.

studied in Uppsala has recently been undertaken and this survey also demonstrates quite clearly that the maximum density is not found precisely in the planes defined by the first coordination sphere. It should therefore be stressed that in discussing the electron densities around the nickel ion in the crystal field, the field from the *whole* crystalline environment must be considered, not just from the nearest neighbours in the first coordination sphere.

Maslen, Ridout & Watson (1988) attributed the deviations from ideal octahedral symmetry observed in their difference maps of $\text{NH}_4\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ to the distinctly planar geometry of the second coordination sphere of Ni. The same explanation was offered by Hester, Maslen, Glazer & Stadnicka (1993) for the deviations in the $X - N$ maps of tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. While we do question the reliability of difference and $X - N$ maps as opposed to deformation model maps, particu-

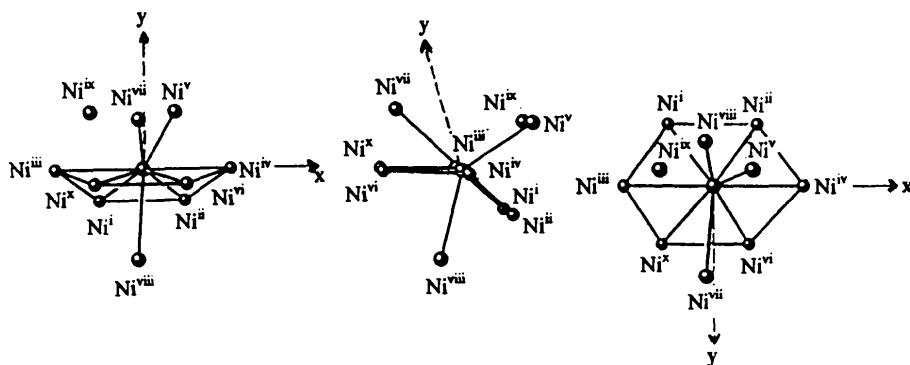


Fig. 6. Three projections of the nickel-nickel arrangement in $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (the y axes are not in the plane of the paper). *cf.* Table 4.

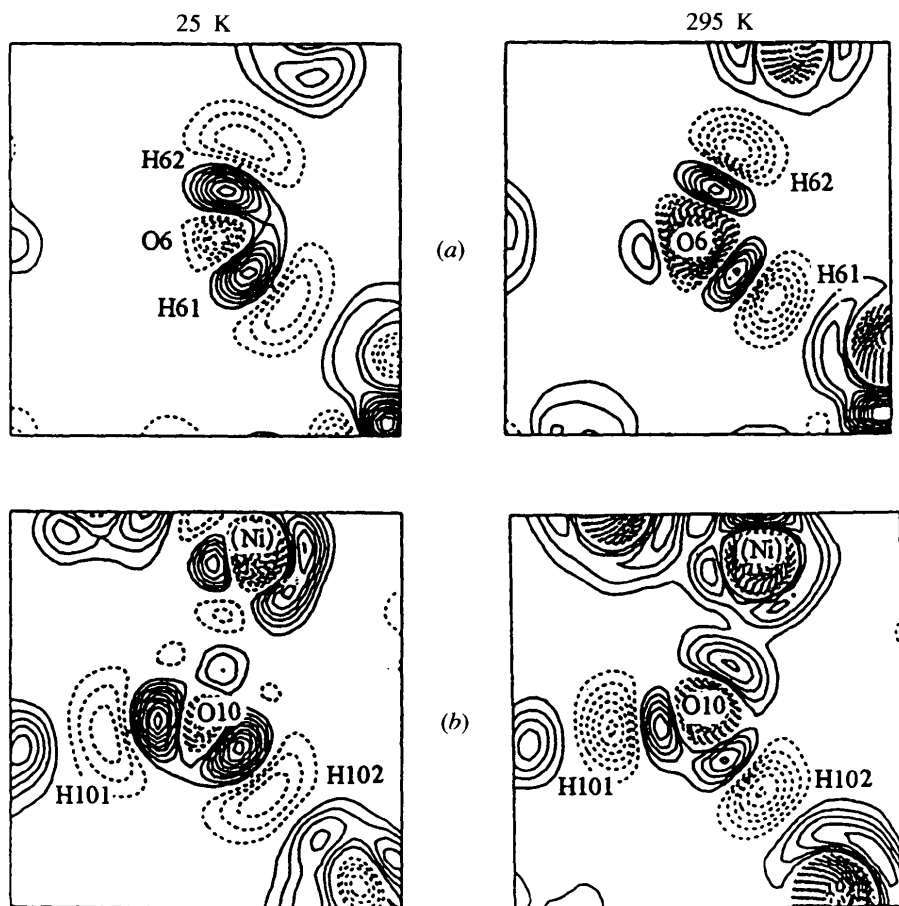


Fig. 7. Deformation densities in the planes of water molecules containing O6 and O10 at 25 and 295 K: (a) and (b) total maps.

larly for non-centrosymmetric structures such as tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and orthorhombic $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, the hypothesis that the second coordination sphere has an important influence does bear careful consideration. Our present study strongly supports this idea. We should, however, be wary of overly interpreting the deformation densities. It should be remembered that they illustrate relatively small fitted deviations from the predominantly spherical symmetry of the atoms, which in our model are complete neutral atoms of the element concerned. The model maps in $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ (Kellersohn, Delaplaine, Olovsson & McIntyre, 1993) gave a more striking example of large deviations from a perfectly octahedral deformation.

In the case of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ it was suggested that the pronounced difference observed between the room temperature and 25 K maps could be due to different occupation of the two upper partially occupied electronic levels. This suggestion was supported by a Boltzmann statistical analysis based on the energy difference experimentally observed in magnetic susceptibility measurements (Ptasiewicz-Bak, Olovsson & McIntyre, 1993).

4.1.2. *The water molecules.* The total deformation densities are illustrated in Fig. 7 in the planes of the water molecules containing O6 and O10 and are perpendicular to those in Fig. 8. These molecules

have been selected as representatives for molecules which are tetrahedrally and trigonally coordinated to nickel, respectively. The maps for the other water molecules have similar features. The superposition effects are again less pronounced in this compound compared with $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. The general features of the densities in the O—H bonds and the lone-pair regions were discussed in a previous paper (McIntyre, Ptasiewicz-Bak & Olovsson, 1990). The most interesting special features are found in the lone-pair planes: in water(6) there are two well-separated 'lone-pair peaks', whereas there is just one peak in water(10), although the single peak is elongated at 25 K. In the free water molecule there is just one 'banana-shaped' peak according to theoretical *ab initio* calculations (Hermansson, 1984). The clear splitting in water(6) is then most probably due to the polarizing influence of the neighbours, effects which are normally considered too small to be observed experimentally. Similar clear polarization of the lone-pair densities according to the coordination of the water molecules was also observed in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.

5. Conclusions

In general, the same conclusions can be drawn from this study as from our earlier experimental charge-density

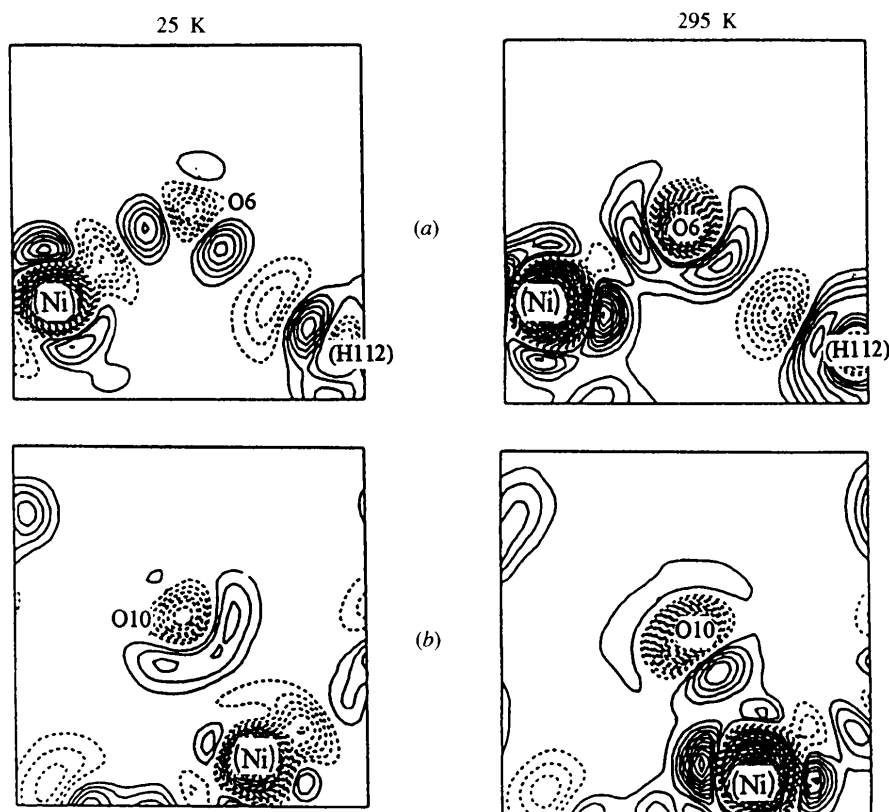


Fig. 8. Deformation densities perpendicular to the planes of water molecules containing O6 and O10, through the twofold axes, at 25 and 295 K: (a) and (b) total maps.

studies of tetragonal NiSO₄·6H₂O, *i.e.* the deformation around Ni follows crystal field theory, details of the deformation in and around water molecules can be extracted, even in the presence of such strong X-ray scatterers as Ni, and the water molecules exhibit polarization that depends on their local environment. The deformation around Ni does appear to be very sensitive to small deviations from a perfectly octahedral environment and to the influence of the *whole* crystalline environment.

We can also conclude that water molecules with the same local coordination are largely transferable and that, lacking neutron data, a reasonable picture of the deformation can be obtained by extrapolating from the refined H coordinates of the conventional refinement. This does assume that there is no disorder or anharmonicity.

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