

## Crystal Structure of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at Room Temperature and $4.2^\circ\text{K}$ by Neutron Diffraction

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## DISCUSSION

The results obtained in this work indicate that the capture-recapture approach can be used to advantage to obtain estimates of the size of the population of polygons weakly embeddable in a lattice. The method is applicable in the size range just beyond the region amenable to exact enumeration, though the application to larger polygons would necessitate the imposition of additional stratification. The method is applicable to

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## ACKNOWLEDGMENTS

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Crystal Structure of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  at Room Temperature and 4.2°K by Neutron Diffraction\*

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Atomic parameters in paramagnetic  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  have been determined at room temperature from a single-crystal neutron-diffraction study in which the intensities of 100 independent reflections of the  $h0l$  and  $hk0$  zones were measured. Isotropic least-squares refinement of the structure gave a final value of 0.104 for the reliability factor  $R$  and yielded the hydrogen parameters  $x, y, z, = (0.100, 0.299, 0.269); (0.444, 0.232, 0.225); (0.181, 0, 0.549);$  and  $(0.260, 0, 0.839)$ . Parameters for the heavy atoms agree with the results of the x-ray structure analysis. Atomic parameters were also determined for the antiferromagnetic state ( $T_N = 5.3^\circ\text{K}$ ) at 4.2°K from 108  $h0l$  reflections. Final  $R$  after isotropic least-squares refinement is 0.070, and a comparison of the two sets of atomic parameters shows that the crystal structure is the same at both temperatures. At 4.2°K the hydrogen parameters are  $(0.107, *, 0.280); (0.441, *, 0.227); (0.184, 0, 0.549);$  and  $(0.261, 0, 0.828)$ , and the unit-cell parameters are  $a = 10.20, c = 6.50 \text{ \AA}$ , and  $\beta = 122^\circ 32'$ .

## INTRODUCTION

In recent nuclear magnetic resonance experiments the magnetic fields at the proton sites in antiferromagnetic  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  have been measured.<sup>1</sup> Subsequent attempts to calculate these local fields on the basis of a simple dipole model, and thereby explain the results of the NMR experiment, were unsuccessful. The calculations were performed using the assumptions: that the fields were dipolar in origin; that the crystal structure in the antiferromagnetic state was the same as that determined at room temperature by x rays<sup>2</sup>; that hydrogen positions in the antiferromagnetic state were the same as those determined in  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  at room temperature and 77° by means of NMR<sup>3</sup>; that the spin direction determined by the susceptibility experiment was correct<sup>4</sup>; and that the magnetic space group

was one of the two possible groups derived from the measured local magnetic fields.<sup>1</sup>

Since these calculations required the use of several assumptions about the magnetic and crystal structures of the material, it was decided to experimentally determine the magnetic structure and spin direction in the antiferromagnetic state, as well as the crystal structure in the paramagnetic and antiferromagnetic states by means of neutron-diffraction experiments, before attempting a more extensive calculation of the local magnetic fields. The magnetic structure has already been discussed in a previous paper.<sup>5</sup> This work is concerned with the crystallographic properties at room temperature and at 4.2°K.

The room-temperature data were taken in two stages, at two different laboratories. Data on the  $h0l$  zone were taken at the U.S. Naval Research Laboratory, and the  $hk0$  data were collected at the Puerto Rico Nuclear Center. From the results of these data it does not appear that a crystallographic change should accompany the magnetic transition at 5.3°K, from the paramagnetic to antiferromagnetic states. Nevertheless, since the magnetic properties of interest had been measured in the range of liquid-helium temperatures,<sup>2-4</sup> it seemed desirable to confirm the crystal

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<sup>1</sup> R. D. Spence, P. Middents, Z. M. El Saffar, and R. Kleinberg, *J. Appl. Phys. Suppl.* **35**, 854 (1964).

<sup>2</sup> J. Mizuno, *J. Phys. Soc. Japan* **16**, 1574 (1961).

<sup>3</sup> Z. M. El Saffar, *J. Phys. Soc. Japan* **17**, 1334 (1962).

<sup>4</sup> R. B. Flippen and S. A. Friedberg, *J. Appl. Phys. Suppl.* **31**, 338 (1960).

<sup>5</sup> R. Kleinberg, *J. Appl. Phys.* **38**, 1453 (1967).

structure at 4.2°K, with a set of data from at least one zone. Further, with reduced thermal motion, it was hoped to obtain more accurate positional parameters at the lower temperature.

Of the eight atom types in the formula unit, five are situated in the (010) mirror plane, leaving only three atoms of a single water molecule with undetermined  $y$  parameters. Thus data were taken on the  $h0l$  zone, from which all atomic  $x$  and  $z$  parameters were determined, leaving only the three  $y$  parameters to be deduced from bond-length considerations. The complete set of low-temperature data was taken at the U.S. Naval Research Laboratory.

TABLE I. Comparison of parameters in  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  determined from: anisotropic least-squares refinement of room-temperature x-ray data; isotropic refinement of room-temperature neutron data; and isotropic refinement of 4.2°K neutron data.

	$x$	$y$	$z$	$B$
Ni	0	0	0	1.8(2) 0.7(1)
Cl	0.2708(2) <sup>a,b</sup>	0	0.1674(3)	1.5(1) 0.8(1)
	0.2691(8)		0.167(1)	
	0.2720(5)		0.1700(7)	
O <sub>I</sub>	0.0307(4)	0.2072(7)	0.2503(6)	2.7(2)
	0.0296(7)	0.203(2)	0.244(1)	1.0(1)
	0.0320(3)		0.2525(5)	
O <sub>II</sub>	0.2825(7)	0	0.7023(11)	2.3(2)
	0.281(1)		0.696(2)	0.9(1)
	0.2823(6)		0.700(1)	
H1	0.100(1) <sup>a</sup>	0.299(3)	0.269(2)	3.5(3)
	0.107(1)		0.280(1)	2.1(1)
H2	0.444(1)	0.232(4)	0.225(2)	3.4(3)
	0.441(1)		0.227(1)	2.3(1)
H3	0.181(4)	0	0.549(5)	5.9(7)
	0.184(1)	0	0.549(2)	2.0(2)
H4	0.260(2)	0	0.839(4)	1.2(4)
	0.261(2)	0	0.828(2)	1.7(2)

<sup>a</sup> Throughout this paper the standard deviation of a function is given in the parenthesis following the function, and its value corresponds to the least significant digits in the function value.

<sup>b</sup> In each heavy atom set of numbers the upper, middle, and lower number subsets correspond to positions determined by: x rays at room temperature; neutrons at room temperature; and neutrons at 4.2°K, respectively.

<sup>c</sup> In each hydrogen atom set of numbers, the upper and lower subsets correspond to positions determined by neutrons at room temperature and 4.2°K, respectively.

## X-RAY DATA

The heavy-atom structure of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  has been determined at room temperature by Mizuno.<sup>2</sup> The unit cell is monoclinic, with space group  $C2/m$ , and contains two formula units per unit cell. Cell dimensions are  $a=10.23$ ,  $b=7.05$ ,  $c=6.57$  Å, with  $\beta=122^\circ 10'$ . The general position is eightfold with equivalent sites at  $x, y, z; x, \bar{y}, z; \bar{x}, y, \bar{z}; \bar{x}, \bar{y}, \bar{z}; 1/2+x, 1/2+y, z; 1/2+x, 1/2-y, z; 1/2-x, 1/2+y, \bar{z}; 1/2-x, 1/2-y, \bar{z}$ . The nickel ions are situated on  $2/m$  inversion centers at the cell corners, and at the centers of the (001) faces. They are each octahedrally coordinated to four oxygen and two chlorine atoms. The oxygens form a slightly distorted square, with the nickel at the center, while the chlorines are located on the two normals to the oxygen plane. The remaining two water molecules of the formula unit are located in the mirror plane and are relatively free, but do take part in the hydrogen-bonding scheme.

Since the atomic parameters given by Mizuno were apparently determined by Fourier and difference Fourier projections, his combined data were refined by full-matrix least squares using anisotropic temperature factors, and weights  $w=(F_0+0.02F_0^2)^{-1/2}$ . A total of 220 independent nonzero and eight duplicate reflections from the  $h0l$ ,  $0kl$ , and  $h1l$  zones were used to obtain the atomic parameters given in Table I. The only parameter which differs from the results of the Fourier method is  $x(\text{O}_{II})$ . Mizuno's value for this parameter is 0.288. The reliability factor  $R=\sum ||F_0|-|F_c||/\sum |F_0|$  is 0.093 after 10 cycles.

## EXPERIMENTAL

Large crystals of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  were grown from aqueous solution at about 30°C, and had the habit described by Groth.<sup>6</sup> A single well-formed crystal of tabular habit, and elongated along the  $b$  axis was used for the  $h0l$  zone work at room temperature. It had the approximate dimensions: effective diameter  $\sim 3.7$  mm; length  $\sim 7$  mm. For the  $hk0$  data, a rather stubby but well-formed crystal was ground into a cylinder with  $c$  as axis, by slowly rubbing the crystal over a damp cotton cloth. The obtained cylinder had the dimensions: diameter was 3.8 mm; length was 5 mm. The crystals were glued to an aluminum mount and protected from the atmosphere by means of a thin-walled titanium-zirconium cap, sealed with silicone grease. Under these conditions they remained stable during the experiment.

The low-temperature experiment was performed on the same crystal used for the room-temperature work on the  $h0l$  zone, except that a slice of it had been accidentally cleaved off along the easy direction. The result was to give a sample of approximately rhombic cross section which had the approximate dimensions: length  $\sim 7$  mm; effective diameter  $\sim 3$  mm. This crystal was

<sup>6</sup> P. Groth, Chem. Kryst. 1, 247 (1906).

TABLE II. Observed and calculated structure factors for  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  at room temperature.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>calc</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>calc</sub>
0	2	0	5.99	6.49	0	0	4	1.01	1.00
0	4	0	3.71	3.43	2	0	-5	2.68	3.43
0	6	0	5.71	5.56	2	0	-4	2.72	2.57
0	8	0	1.73	2.16	2	0	-3	1.85	1.63
0	10	0	3.66	3.29	2	0	-2	3.55	3.56
1	1	0	2.75	2.96	2	0	-1	1.53	1.66
1	3	0	5.04	-4.81	2	0	1	0.73	-0.09
1	5	0	6.99	6.39	2	0	2	3.84	4.38
1	7	0	3.03	-3.01	2	0	3	1.95	2.44
1	9	0	2.03	2.04	2	0	4	2.92	3.63
2	0	0	0.76	-0.26	4	0	-4	1.01	0.97
2	2	0	1.95	-1.98	4	0	-3	1.93	-1.79
2	4	0	1.62	-1.76	4	0	-1	6.64	5.78
2	8	0	2.34	-2.41	4	0	1	1.78	-1.71
3	1	0	5.81	6.20	4	0	2	6.48	-7.41
3	3	0	2.16	2.45	4	0	3	2.76	3.41
3	5	0	5.98	6.29	6	0	-6	2.17	-2.52
3	9	0	2.53	2.78	6	0	-5	7.45	8.36
3	11	0	1.20	1.24	6	0	-4	8.56	7.90
4	0	0	9.57	9.84	6	0	-3	3.98	-3.85
4	2	0	1.20	1.60	6	0	-2	5.96	-5.11
4	4	0	5.98	5.61	6	0	-1	7.98	7.82
4	6	0	4.60	4.48	6	0	1	3.10	-2.73
4	8	0	2.01	1.33	6	0	2	1.50	1.76
4	10	0	3.85	3.03	8	0	-8	1.19	2.01
5	1	0	2.27	-2.08	8	0	-6	1.94	2.38
5	3	0	2.00	-1.59	8	0	-5	5.16	5.19
6	0	0	3.05	3.16	8	0	-4	1.65	-1.75
6	2	0	3.85	-4.07	8	0	-3	5.51	-4.44
7	1	0	4.93	4.72	8	0	-2	4.27	3.89
7	3	0	4.60	4.62	8	0	-1	8.15	7.63
7	5	0	3.68	3.55	8	0	1	2.90	-3.38
7	7	0	2.89	3.24	10	0	-9	1.35	1.95
7	9	0	1.98	2.01	10	0	-7	2.70	-3.08
8	0	0	3.69	3.57	10	0	-6	1.30	1.60
8	2	0	1.74	1.27	10	0	-5	6.78	6.07
8	4	0	3.41	2.89	10	0	-4	5.62	4.60
8	6	0	1.20	0.99	10	0	-3	1.82	-1.80
8	8	0	1.48	1.50	10	0	-2	1.13	-1.53
9	3	0	1.72	-1.45	10	0	-1	1.54	1.46
10	4	0	1.66	1.41	10	0	3	1.03	1.76
10	8	0	1.62	1.37	12	0	-7	1.73	1.50
11	1	0	2.71	2.93	12	0	-4	3.66	-3.34
11	3	0	3.21	3.08	12	0	-3	1.97	1.48
11	5	0	1.54	2.14	12	0	-2	5.58	5.35
11	7	0	2.35	2.27	12	0	-1	2.54	2.63
14	2	0	2.53	2.03	14	0	-8	2.06	-2.48
0	0	1	4.19	3.80	14	0	-6	2.74	2.33
0	0	2	1.29	-1.05	14	0	-5	1.95	2.02
0	0	3	1.65	1.77	14	0	-4	2.39	2.47

suspended from a titanium-zirconium crystal mount that was attached to the tail of the helium chamber of a Hofman Dewar. Silicone grease was used as the adhesive.

Unit cell parameters were determined by measuring the coordinates of at least 18 reciprocal lattice points for each zone, ranging from  $10^\circ$  to  $73^\circ$  in two-theta, and then finding the parameters which gave the best least-squares fit between the measured and calculated coordinates. The quantities minimized were  $[\sum \theta_0(2\theta_0 - 2\theta_c)^2 / \sum \theta_0]^{1/2}$  and  $[\sum (\phi_0 - \phi_c)^2]^{1/2}$ . Parameters determined by this procedure are  $a = 10.24$ ,  $b = 7.04$ ,  $c = 6.58$  Å, and  $\beta = 122^\circ 14'$  at room temperature, and  $a = 10.20$ ,  $c = 6.50$  Å, and  $\beta = 122^\circ 32'$  at  $4.2^\circ\text{K}$ . The room-temperature parameters are in good agreement with those determined by x rays. Observed extinctions for both zones are in accordance with the space group  $C2/m$  given by Mizuno.

Intensity measurements at room temperature yielded 53 observed independent  $h0l$ , and 47 observed independent  $hk0$  reflections, which gave a total of 100 independent observed reflections. A reflection was defined to be unobserved, when from counting statistics the intensity was less than three times its standard deviation. Measurements were made for theta less than  $50^\circ$ .

At  $4.2^\circ\text{K}$ , intensity measurements were made for theta less than  $60^\circ$ , and a total of 108 reflections were observed. A reflection was considered unobserved when its intensity was less than four times its standard deviation.

Since the incoherent scattering from hydrogen is large, cylindrical absorption corrections, determined from Table 5.35B in the *International Tables for X-Ray Crystallography*,<sup>7</sup> were applied to the intensities in both sets of data. A value of  $\sum R = 0.904$  was used. Extinction was judged to be unimportant, and no correction was made, but as described below, a least-squares weighting scheme was used which accounted for the possible occurrence of this effect.

## REFINEMENT OF THE STRUCTURE

All intensity data were refined by full-matrix least squares based on  $F$ , using the Los Alamos Crystal Structure Least-Squares Program, GENLES.<sup>8</sup> Scattering lengths were taken as constant, and were assumed to be 1.03, 0.960, 0.577, and  $-0.374$  ( $\text{cm} \times 10^{-12}$ ) for Ni, Cl, O, and H, respectively. The quantity minimized was  $\sum w ||F_o| - |F_c||^2$ , where  $w = [\sigma(F) + 0.025F]^{-2}$  and  $\sigma(F)$  is the standard deviation of the structure factor as determined from counting statistics. Unobserved reflections were given zero weight, and the weights for

<sup>7</sup> *International Tables for X-ray Crystallography*, K. Lonsdale et al., Eds. (Kynoch Press, Birmingham, England, 1962), Vol. 2.

<sup>8</sup> A. C. Larson (private communication). Operator's Manual for the Los Alamos Crystal Structure Least-Squares Program GENLES.

TABLE III. Observed and calculated structure factors for  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  at 4.2°K.

<i>h</i>	0	<i>l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>calc</sub>	<i>h</i>	0	<i>l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>calc</sub>	<i>h</i>	0	<i>l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>calc</sub>
0		1	3.64	3.94	4		8	*	1.00	10		-2	1.46	-1.50
0		2	1.51	-1.38	6		-11	*	0.99	10		-1	2.13	2.22
0		3	1.99	2.05	6		-10	1.99	2.31	10		0	*	0.46
0		4	1.84	1.64	6		-9	4.26	4.08	10		1	1.95	2.03
0		5	1.16	1.20	6		-8	4.11	3.94	10		2	4.94	5.11
0		6	2.57	2.78	6		-7	4.58	-4.57	10		3	3.74	3.75
0		7	2.95	3.37	6		-6	5.37	-5.25	10		4	2.97	-3.35
0		8	1.76	1.75	6		-5	10.40	10.37	12		-11	4.00	-3.64
0		9	*	-1.50	6		-4	10.27	10.11	12		-10	*	-0.43
2		-10	*	-0.14	6		-3	4.33	-4.13	12		-9	5.00	4.64
2		-9	4.56	4.13	6		-2	6.78	-6.63	12		-8	3.02	2.47
2		-8	4.40	3.67	6		-1	9.18	9.38	12		-7	1.96	1.81
2		-7	*	-0.74	6		0	3.35	3.31	12		-6	3.46	3.41
2		-6	3.10	-2.56	6		1	4.08	-4.11	12		-5	*	0.85
2		-5	4.71	4.55	6		2	2.76	2.78	12		-4	5.56	-5.55
2		-4	3.31	3.15	6		3	8.09	8.72	12		-3	2.83	2.48
2		-3	1.84	1.90	6		4	*	0.50	12		-2	7.53	7.85
2		-2	3.36	3.45	6		5	4.52	-4.68	12		-1	3.03	3.60
2		-1	1.53	1.46	6		6	*	0.77	12		0	1.77	-2.20
2		0	0.56	0.11	6		7	2.84	3.63	12		1	*	-0.40
2		1	0.74	-0.59	8		-11	4.13	-3.65	12		2	*	1.22
2		2	4.44	4.48	8		-10	2.81	-2.90	14		-11	3.68	3.40
2		3	3.19	3.42	8		-9	7.14	6.64	14		-10	7.13	5.98
2		4	5.22	5.41	8		-8	4.05	3.58	14		-9	*	0.12
2		5	1.19	-1.20	8		-7	1.64	-1.65	14		-8	4.85	-4.49
2		6	3.31	-3.69	8		-6	2.26	2.17	14		-7	*	1.14
2		7	*	1.69	8		-5	7.01	6.68	14		-6	3.97	4.32
2		8	6.68	6.66	8		-4	1.51	-1.64	14		-5	1.84	2.25
4		-10	*	-0.44	8		-3	6.00	-5.67	14		-4	3.03	3.11
4		-9	*	1.08	8		-2	5.10	5.36	14		-3	1.41	1.21
4		-8	1.79	1.41	8		-1	9.01	8.77	14		-2	*	-0.71
4		-7	2.34	2.34	8		0	4.13	3.68	14		-1	*	-0.99
4		-6	4.95	5.11	8		1	4.94	-4.71	14		0	*	2.10
4		-5	*	0.61	8		2	1.32	-1.40	14		1	1.84	2.49
4		-4	1.74	1.73	8		3	2.40	2.78	16		-9	*	1.49
4		-3	2.05	-1.96	8		4	4.45	4.60	16		-8	3.97	3.76
4		-2	*	-0.40	8		5	*	1.42	16		-7	2.45	2.20
4		-1	6.54	6.52	10		-11	*	0.35	16		-6	1.36	1.65
4		0	10.04	10.04	10		-10	5.52	5.16	16		-5	*	-0.76
4		1	2.82	-2.72	10		-9	4.93	4.49	16		-4	1.83	-2.61
4		2	8.39	-8.87	10		-8	1.30	-0.67	16		-3	1.83	1.74
4		3	5.54	5.99	10		-7	6.17	-5.68	16		-2	6.88	6.89
4		4	7.40	8.04	10		-6	1.59	1.75	16		-1	2.19	3.12
4		5	*	-0.64	10		-5	8.46	7.71	18		-7	*	1.51
4		6	*	-1.68	10		-4	6.64	6.17	18		-6	6.44	5.64
4		7	4.79	5.30	10		-3	2.41	-2.22					

TABLE IV. Interatomic distances and bond angles in  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  at room temperature and at 4.2°K.

Ni-Cl	2.359(7) <sup>a</sup> 2.366(4)	2.375 <sup>b</sup>	O <sub>I</sub> -O <sub>I</sub> (2)	2.86(1)	2.92 <sup>b</sup>
Ni-O <sub>I</sub>	2.05(1)	2.094	Cl-O <sub>I</sub>	3.10(1)	3.146
Ni-O <sub>II</sub>	3.90(1) 3.853(5)	3.932	Cl-O <sub>II</sub> '	3.73(1)	3.731
O <sub>I</sub> -O <sub>I</sub> (4)	2.93(1) 2.979(5)	3.006	Cl-Cl(4)	4.06(1)	4.053
O <sub>II</sub> -H3	0.96(4) 0.95(1)		O <sub>I</sub> -H1	0.94(2)	
O <sub>II</sub> -H4	1.07(3) 0.97(1)		O <sub>I</sub> -H2'	0.94(2)	
H3-H4	1.63(4) 1.54(2)		H1-H2'	1.48(2)	
O <sub>II</sub> -B	2.70(1) 2.639(5)	2.703	O <sub>I</sub> -O <sub>II</sub> '	2.74(1)	2.715
O <sub>II</sub> -Cl''	3.17(2) 3.109(7)	3.126	O <sub>I</sub> -Cl'	3.21(1)	3.176
B-H3	1.77(2) 1.700(8)		O <sub>II</sub> '-H1	1.80(2)	
Cl''-H4	2.11(3) 2.16(1)		Cl'-H2'	2.30(2)	
O <sub>I</sub> -H3	2.27(2)		O <sub>I</sub> -O <sub>II</sub>	3.06(1)	3.072
H3-O <sub>II</sub> -H4	107°(2) 107(1)		H1-O <sub>I</sub> -H2'	104°(2)	
O <sub>II</sub> -H3-B	165(1) 168(1)		O <sub>I</sub> -H1-O <sub>II</sub> '	174(2)	
O <sub>II</sub> -H4-Cl''	168(1) 166(1)		O <sub>I</sub> -H2'-Cl'	164(2)	
B-O <sub>II</sub> -Cl''	124.7(4) 124(1)	124.4	O <sub>II</sub> '-O <sub>I</sub> -Cl'	89.5(4)	90.7

<sup>a</sup> Upper number in each number set refers to room temperature, lower number to 4.2°K bond or angle.

<sup>b</sup> Bond lengths and angles in these columns were calculated from x-ray data.

the reflections 200 and 201 were adjusted to account for contributions from  $\lambda/2$  scattering. At the end of the refinement  $\Delta\xi_i/\sigma(\xi_i) < 10^{-2}$  for all least-squares parameters  $\xi$ .

For the refinement of the room-temperature data, 27 parameters, including 2 scale factors, 17 atomic

parameters, and 8 isotropic thermal parameters, were determined from the 100 unique reflections. The initial input parameters were the heavy-atom parameters given by Mizuno, and the hydrogen positions proposed for  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  by El Saffar.<sup>8</sup> At the end of refinement the reliability factor  $R = \sum |\Delta F| / \sum |F_0|$ ,

for the observed reflections was 0.104. Final positional and isotropic thermal parameters with their calculated standard deviations are listed in Table I, and the observed and calculated structure factors are given in Table II.

A second isotropic refinement was made in which the heavy atoms were held fixed in the positions determined from the x-ray data, and given in Table I. For the 10 hydrogen parameters determined by this procedure, eight are within one standard deviation, and two are within two standard deviations of the values obtained from the first refinement. The final  $R$  is 0.117, and the maximum shift in hydrogen atomic parameter is 0.031 Å.

For the low-temperature refinement 23 parameters (1 scale, 14 atomic, and 8 isotropic thermal) were determined from the 108 reflections, yielding a final value of  $R=0.0702$  for observed reflections. Initial input parameters were the ones determined at room temperature, and the final positional and isotropic thermal parameters are listed in Table I. The observed and calculated structure factors are given in Table III, where unobserved reflections are designated by an asterisk.

A second refinement was made using data which had not been corrected for absorption. The reliability factor obtained from this refinement is 0.0814, and the maximum shift in atomic parameter, from those given in Table III, is 0.001 or 0.010 Å.

### DISCUSSION

Comparing the heavy-atom positions in Table I, determined by means of x rays, and neutrons at room temperature, we note that the chlorine positions are in good agreement, but that the oxygens are not. All the parameter differences, except one, are within  $3\sigma(\text{ND})$ , and they are interpreted as due to systematic errors such as the "smearing out" of atomic positions, and parameter overlap due to large thermal motion and lack of three-dimensional data. Accordingly, these differences serve as a measure of the accuracy of the neutron experiment, as opposed to indicating a real discrepancy between the results of the two experiments.

The positions of the heavy atoms measured at 4.2°K are in excellent agreement with the room-temperature x-ray results. The largest parameter difference for the

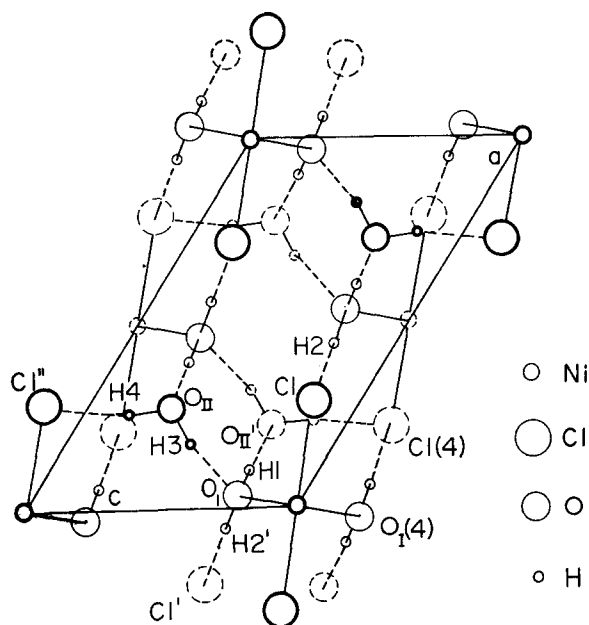


FIG. 1. A representation of the crystal structure of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  viewed along the  $b$  axis. Heavy-lined and dashed circles represent atoms in the mirror planes  $y=0$  and  $y=\frac{1}{2}$ , respectively. Thin-lined circles represent atoms at  $0 < y < \frac{1}{2}$ . Hydrogen bonds are represented by dashed lines.

heavy atoms is 0.003 or 0.017 Å, while for the hydrogen atoms the largest difference between a 4.2°K and a corresponding room-temperature parameter is 0.072 Å. The fact that the  $x$  and  $z$  parameters of all the atoms agree so well with the room-temperature positions indicates that no rearrangement occurs at low temperatures. Thus the crystal structure of the antiferromagnetic state at 4.2°K is the same as in the paramagnetic state at room temperature.

Accordingly, the  $y$  parameters for the atoms in the water molecule in the general position, which were not measured at 4.2°K, may be deduced approximately from bond-length considerations. If an arbitrary value of 6.99 Å is assumed for the unmeasured unit cell parameter  $b$ , and  $y(\text{O}_I)$  is selected to give a Ni–O<sub>I</sub> bond distance of 2.091 Å, and if proton positions are selected to give visually reasonable values for the water molecule geometry and for the hydrogen-bond distances, then the  $y$  parameters 0.210, 0.308, and 0.228 are obtained for the O<sub>I</sub>, H<sub>1</sub>, and H<sub>2</sub> atoms, respectively.

Some bond lengths and angles calculated from the observed atomic parameters are given in Table IV. Values calculated from the x-ray determination are also given, and as expected the agreement is good except for O<sub>I</sub>–O<sub>I</sub>-type bonds at room temperature.

The apparent exceptional length of the O<sub>II</sub>–H<sub>4</sub> bond at room temperature is due to overlap in projection between Cl<sub>1</sub> and H<sub>4</sub> atoms in adjacent mirror planes, as for example Cl<sub>1</sub> at (0.229, 0.5, 0.833) and H<sub>4</sub> at (0.260, 0, 0.839). On the other hand, the O<sub>I</sub>–H bonds appear to be somewhat short, with "riding" motion corrections

TABLE V. Proton-proton vectors in  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ .

Vector	$\alpha_0$	$\beta_0$	$\gamma_0$	$r$	Salt	
I	16.0°	80.0°	110.0°	1.57 Å	Co	NMR
	13.2	81.5	112.3	1.48	Ni	ND
II	96.0	90.0	26.0	1.62	Co	NMR
	97.5	90.0	24.7	1.63	Ni	ND

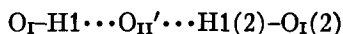
of only 0.01 Å.<sup>9</sup> But, since the standard deviations are so large it is difficult to attribute this effect to a large librational motion of the water molecule. Other bonds and angles are in agreement with previously reported results.<sup>10-12</sup> The Ni-Cl<sub>I</sub> and O<sub>I</sub>-O<sub>I</sub>(4) distances of 2.366 and 2.979 Å, respectively, observed at 4.2°K, when compared to the distances of 2.375, and 3.006 Å observed at room temperature, indicate again that no molecular rearrangement has occurred in the NiCl<sub>2</sub>·4H<sub>2</sub>O molecule, on entering the antiferromagnetic state.

Since all of the atomic parameters of the free water molecule were observed, it is of interest to examine the molecular and hydrogen-bond lengths of this molecule. The oxygen-hydrogen bonds (uncorrected for "riding" motion) are 0.95 and 0.97 Å, with an enclosed H-O-H angle of 107°. The O<sub>II</sub>-Cl'' distance is 3.11 Å, and the H4...Cl'' hydrogen bond distance is 2.16 Å. These numbers compare favorably with the corresponding room-temperature results and also with previously tabulated values.<sup>12,13</sup>

A projection of the structure along the *b* axis, onto the mirror plane is given in Fig. 1, wherein most of the atomic symbols are defined, and the hydrogen-bonding scheme is indicated.

In the hydrogen-bonding system, H3 has a bifurcated-type bond with O<sub>I</sub> and its mirror image O<sub>I</sub>(2), but it is interesting to note that H3 appears to be hydrogen bonded to the point B, the midpoint between O<sub>I</sub> and O<sub>I</sub>(2). The distances for H3...B, and O<sub>II</sub>-H3...B of 1.77 and 2.70 Å, are essentially the same as the corresponding distances of 1.80 and 2.72 Å, associated with O<sub>I</sub>-H1...O<sub>II</sub>'. Curiously enough, if the hydrogen bond is essentially electrostatic, having effective point charge *q* on each oxygen atom, then O<sub>I</sub> and O<sub>I</sub>(2) may be replaced by an imaginary charge of 1.5*q* at the point B. This would seem to imply that the bifurcated bond is not necessarily a weak one.

The crystal structure is determined by hydrogen bridges of the type



and



[where H1(2), H2'(2), and O<sub>I</sub>(2) are the mirror

images of H1, H2', and O<sub>I</sub>, respectively] which link the NiCl<sub>2</sub>·4H<sub>2</sub>O octahedra into a face-centered two-dimensional network parallel to the (001) plane, and bridges of the type



which bond together the neighboring two-dimensional networks. Hydrogen atoms from each O<sub>I</sub> water molecule enter into two hydrogen bridges which are essentially "parallel," while those from each O<sub>II</sub> water molecule enter into bonds which are essentially "collinear" in their effect on the crystal structure. Thus there are only half as many structural bridges along the (001) as along other directions, and this results in the perfect cleavage parallel to the (001) plane.

Proton-proton vectors for CoCl<sub>2</sub>·6H<sub>2</sub>O in the paramagnetic state have been measured by El Saffar, using the NMR method.<sup>3</sup> Since this salt is isomorphous to NiCl<sub>2</sub>·6H<sub>2</sub>O, with respect to the heavy atoms, it is of interest to compare his results to those calculated from the hydrogen parameters presented above. Thus *p*-*p* vectors determined from the NMR and neutron-diffraction experiments are given in Table V, where *r* is the *p*-*p* separation, and α<sub>0</sub>, β<sub>0</sub>, and γ<sub>0</sub> are the angles that a vector makes with the *a*, *b*, and *c* axes, respectively. The agreement is quite good, except for small differences in the *r*, which are probably due to the small errors in the atomic positions. Thus, these salts are probably also isomorphous with respect to the hydrogen atoms.

This investigation was undertaken to locate the hydrogen atoms in the paramagnetic and antiferromagnetic states of NiCl<sub>2</sub>·6H<sub>2</sub>O. It has resulted in a determination of the hydrogen positions, and a confirmation of the hydrogen-bonding scheme proposed by El Saffar for CoCl<sub>2</sub>·6H<sub>2</sub>O. It has also shown that the crystal structure is the same in both magnetic states.

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