

computers of the Computing Centres of Nagoya and of Kyoto University using the two programs: *ATLS* (block-diagonal least-squares refinement, by A. Furu-saki and others at Kwansei Gakuin University) and *RSDA4* [bond lengths and angles, Sakurai (1967)].

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Structure Determination of Pentaquocopper(II) Tetrafluoroberyllate

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The crystal and molecular structure of $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$ was determined by single-crystal X-ray analysis. Crystals of $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$ are triclinic, space group $P\bar{1}$. The title compound is isomorphous with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Cell parameters are $a = 7.132$ (1), $b = 10.674$ (1), $c = 5.924$ (4) Å, $\alpha = 97.53$ (3), $\beta = 125.49$ (5), $\gamma = 93.94$ (5)°. The unit cell contains two molecular units with Cu atoms on centres of symmetry 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Least-squares refinement resulted in $R = 0.0197$ and $R_w = 0.0281$ for 3494 observed reflexions. The Cu atoms are surrounded by four O (± 1.96 Å) and two F atoms (± 2.35 Å) in approximate D_{4h} symmetry. Be is tetrahedrally surrounded by four F atoms (± 1.55 Å). The molecular structure consists of chains of alternating octahedra and tetrahedra along [111]. The octahedra and tetrahedra are coupled *via* F atoms. Special attention is given to corrections for absorption and extinction phenomena. Possibilities such as disorder and the non-centrosymmetric space group are discussed.

Introduction

Crystal structures of several compounds closely related to $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$ have been reported ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Beevers & Lipson, 1934; Bacon & Curry, 1962; $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$, Baur & Rolin, 1972; $\text{MgCrO}_4 \cdot 5\text{H}_2\text{O}$, Bertrand, Dusausoy, Protas & Wattle-Marion, 1971). The isomorphism of $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$ with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was reported by Tedenac, Granier, Norbert & Cot (1969). Cell constants for $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$ were calculated by Avinens, Cot & Maurin (1970) from Debye-Scherrer photographs. Their reported values ($a = 7.146$ (3), $b = 10.685$ (3), $c = 5.942$ (3) Å, $\alpha = 97.47$ (3), $\beta = 125.57$ (3), $\gamma = 94.00$ (3)°) are in reasonable agreement with our results (Table 1).

The magnetic behaviour of copper ions (Soda & Chiba, 1969) in this structural type is very interesting due to the presence of two different magnetic systems, one being paramagnetic, the other anti-ferromagnetic. A further exploration of the magnetic properties was

made by Henkens, Diederix, Klaassen & Poulis (1975) who studied $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$ by means of n.m.r. investigations on Be ($I = 1$) and F ($I = \frac{1}{2}$) at about 1 K.

Proton magnetic resonance spectra showed differences between this compound and the sulphate. This prompted us to undertake a detailed crystallographic study. Corrections for absorption and extinction effects were made carefully, to reduce systematic errors. A fairly good solution of the structure in space group $P\bar{1}$ has been determined, which shows no significant deviations from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, contrary to the evidence from the n.m.r. data. In the discussion, attention is given to possible deviations from the structure presented suggested by the observed anomalous p.m.r. spectra.

Experimental

Crystal data and technical information are collected in Table 1. Preliminary investigations concerning

quality and orientation of the crystal were carried out by means of Weissenberg photographs.

The unit cell was chosen according to Delauney's rules (*International Tables for X-ray Crystallography*, 1952). Transformation matrices to convert our data to the system given for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Bacon & Curry, 1962) are **S** and **T**, for axes and coordinates respectively:

$$\mathbf{S} = (\bar{1}, 0, \bar{1}; 0, \bar{1}, 0; 0, 0, 1),$$

$$\mathbf{T} = (\bar{1}, 0, 0; 0, \bar{1}, 0; \bar{1}, 0, 1).$$

A crystal $0.16 \times 0.40 \times 0.50$ mm was selected and mounted with the ϕ axis of the instrument normal to $(\bar{2}31)$. Reflexion intensities were recorded at room temperature with a three-circle single-crystal diffractometer, using graphite-monochromatized $\text{Mo } K\alpha$ radiation.

A lower limit of twice the standard deviation $\sigma(I)$ of the intensity measurements was adopted for the observed reflexions. The values of these σ 's were calculated from the statistical variance of the measurements, taking into account errors in the applied absorption correction and in factors for attenuation filters. Unobserved and non-significant reflexions

were omitted from the refinement process, after a number of reflexions were found to be erroneously designated as unobserved because of a fault in the apparatus.

For reasons mentioned in the introduction the correction for absorption has been carried out carefully. We started with an accurate description of the crystal faces for which with a microscope we defined the crystal corners in terms of orthogonal coordinates and a computer program calculated the boundary faces. The identified faces are listed in Table 2. Fig. 1 shows the morphology of the crystal. The distances varied with respect to the origin by an iterative process until a fairly good fit with the actual shape of the

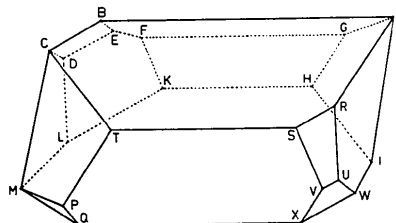


Fig. 1. Morphology of the crystal.

Table 1. *Crystal and technical data for $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$*

<i>a</i>	7.132 (1) Å	Space group	$P\bar{1}$
<i>b</i>	10.674 (1)	<i>Z</i>	2
<i>c</i>	5.924 (4)	d_{calc}	2.212 g cm ⁻³
α	97.53 (3)°	<i>V</i>	358.1 Å ³
β	125.49 (5)	M.W.	238.65 g mol ⁻¹
γ	93.94 (5)	Counting slit	1.25 mm
$\lambda(\text{Mo } K\alpha)$	0.71069 Å	Monochromator	graphite
$\mu(\text{Mo } K\alpha)$	31.1 cm ⁻¹	Measured reflexions	4204
Bragg angle	0–40°	Sign. reflexions	3494
Scan type	$\theta-2\theta$	Non-sign. reflexions	53
Scan angle	0.7° + 0.9° tan θ	Unobs. reflexions	657
Scan speed	1.25° min ⁻¹		

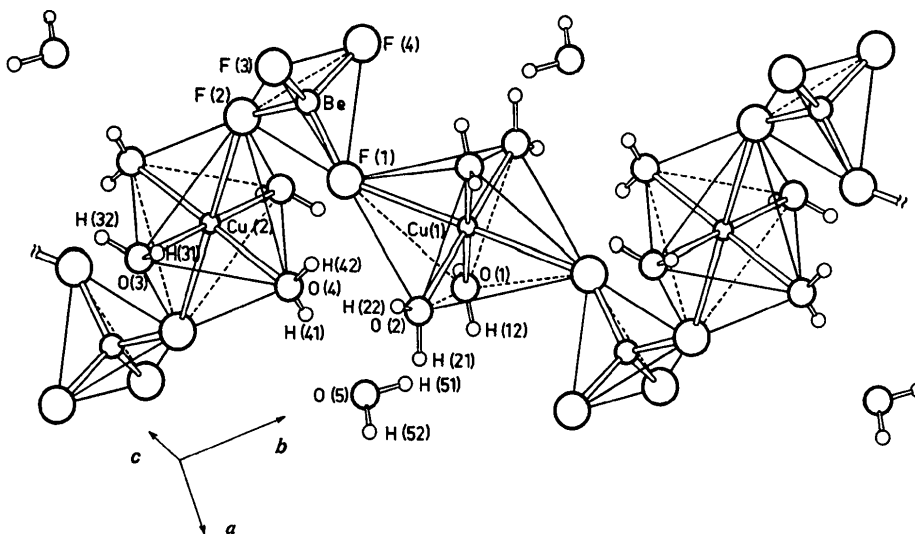


Fig. 2. $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$, part of a chain of tetrahedra and octahedra along $[111]$, together with atomic numbering.

crystal was obtained. The absorption correction was applied using this model as a basis for the program

ABSCOR, developed by de Graaff (1973). Calculated transmission factors are between 0.36 and 0.64. The results of the correction are illustrated with an azimuth scan of reflexion 462 (Table 3).

Table 2. Description of the crystal model for *ABSCOR*

Crystal face	Edges	Distance to origin ($\times 10^2$ mm)
0 1 $\bar{1}$	H K L M Q X W I	7.89
0 $\bar{1}$ 1	A B C T S R	7.75
1 1 0	T S V X Q P	17.38
$\bar{1}$ $\bar{1}$ 0	F G H K	19.03
$\bar{1}$ $\bar{2}$ 1	A B E F G	16.66
1 $\bar{1}$ 0	T P M C	21.28
$\bar{1}$ 1 0	A I H G	22.29
0 $\bar{2}$ $\bar{1}$	D E F K L	20.73
0 2 1	R U V S	23.62
0 1 0	U W X V	27.46
0 $\bar{1}$ 0	B C D E	25.08
1 $\bar{2}$ $\bar{1}$	C D L M	25.83
$\bar{1}$ 2 1	A I W U R	25.13
4 1 $\bar{3}$?	P Q M	30.78

Refinement

After correction for Lorentz and polarization effects the intensities were reduced to F_o values. A Wilson plot was calculated in order to obtain approximate values for the scale factor and overall B .

Scattering factors were taken from Cromer & Waber (1965) for Cu and for the light atoms from Ibers (*International Tables for X-ray Crystallography*, 1962). The scattering of Cu was corrected for both the real and the imaginary part of the anomalous dispersion of Mo $K\alpha$ radiation.

The numbering of atoms is indicated in Fig. 2. The atomic parameters of non-hydrogen atoms of

Table 3. Results of *ABSCOR* for the azimuth scan of reflexion 462

φ	Transm.	$I_{obs} \times 10^{-2}$	Δ_{obs}	$I_{calc} \times 10^{-2}$	Δ_{calc}
0	0.427 (2)	1985 (14)	-14.70	4648	+1.08
15	0.366 (2)	1682 (13)	-27.72	4596	-0.01
30	0.418 (2)	1934 (14)	-16.89	4627	+0.62
45	0.504 (3)	2363 (16)	+1.55	4692	+2.01
60	0.566 (3)	2616 (16)	+12.42	4619	+0.46
75	0.604 (3)	2778 (17)	+19.38	4596	-0.01
90	0.629 (3)	2857 (17)	+22.78	4545	-1.16
105	0.630 (3)	2898 (17)	+24.54	4596	-0.01
120	0.618 (3)	2890 (17)	+24.19	4673	+1.61
135	0.595 (3)	2744 (16)	+17.92	4609	+0.24
150	0.557 (3)	2568 (15)	+10.36	4614	+0.35
165	0.496 (2)	2335 (15)	+0.34	4705	+2.28
180	0.427 (2)	2000 (14)	-14.05	4679	+1.73
195	0.364 (2)	1657 (12)	-28.79	4554	-0.96
210	0.424 (2)	1887 (13)	-18.91	4448	-3.37
225	0.504 (3)	2287 (15)	-1.72	4541	-1.25
240	0.569 (3)	2612 (17)	+12.25	4590	-0.17
255	0.603 (3)	2754 (17)	+18.35	4569	-0.63
270	0.629 (3)	2799 (17)	+20.28	4448	-3.37
285	0.628 (3)	2840 (18)	+22.05	4522	-1.68
300	0.620 (3)	2793 (18)	+20.03	4506	-2.05
315	0.594 (3)	2702 (17)	+16.12	4548	-1.10
330	0.558 (3)	2570 (17)	+10.44	4608	+0.22
345	0.500 (2)	2356 (16)	+1.25	4709	+2.36
360	0.428 (2)	2012 (14)	-13.54	4706	+2.30
Averaged values:		$I_{obs} = 2327$	$\bar{\Delta}_{obs} = 17.87$	$I_{calc} = 4598$	$\bar{\Delta}_{calc} = 1.62$
$I = \sum I_n/n; \Delta = (I - I)/I; \bar{\Delta} = [(\sum \Delta_n^2)/n - 1]^{1/2}$					

Table 4. Fractional coordinates ($\times 10^4$) and anisotropic thermal parameters of non-hydrogen atoms ($U_{ij} \times 10^4 \text{ \AA}^2$)

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
Cu(1)	0	0	0	166 (1)	145 (1)	160 (1)	41 (1)	58 (1)	201 (1)
Cu(2)	5000	5000	5000	130 (1)	172 (1)	118 (1)	85 (1)	43 (1)	148 (1)
Be	124 (2)	2876 (1)	3866 (2)	147 (4)	177 (4)	160 (4)	83 (6)	78 (6)	205 (7)
F(1)	-975 (1)	1464 (1)	2246 (2)	229 (3)	213 (2)	302 (3)	-9 (4)	-88 (4)	312 (5)
F(2)	2568 (1)	3187 (1)	4524 (2)	211 (2)	243 (3)	395 (3)	14 (4)	43 (5)	435 (5)
F(3)	-1555 (1)	3762 (1)	2104 (2)	284 (3)	359 (3)	288 (3)	355 (5)	371 (5)	386 (5)
F(4)	466 (1)	3016 (1)	6749 (2)	274 (3)	316 (3)	174 (2)	178 (4)	109 (4)	299 (4)
O(1)	1812 (1)	-724 (1)	3410 (2)	261 (3)	234 (3)	205 (3)	14 (5)	166 (5)	200 (5)
O(2)	2870 (1)	1200 (1)	1481 (2)	229 (3)	185 (3)	249 (3)	-24 (4)	13 (5)	320 (5)
O(3)	4666 (1)	4078 (1)	1685 (2)	175 (3)	441 (4)	169 (3)	73 (6)	-128 (6)	211 (5)
O(4)	2385 (1)	5807 (1)	2590 (2)	296 (4)	588 (6)	239 (3)	610 (8)	460 (7)	395 (6)
O(5)	4358 (1)	1282 (1)	-1864 (2)	186 (3)	305 (4)	237 (3)	74 (5)	64 (5)	222 (5)

CuSO₄·5H₂O, obtained by Bacon & Curry (1962) and transformed to our crystal system were introduced in the analysis. This resulted in $R=0.089$ and $R_w=0.111$. Least-squares refinement was started at this stage on the basis of space group $P\bar{1}$, with Cu atoms centred on 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The function minimized during the refinement process was: $\sum w(|F_o| - |F_c|)^2$ with weights $w = \sigma_{F_o}^{-2}$. Discrepancy indices are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The full-matrix refinement was performed with the 3494 statistically significant reflexions. The refinement, extended to H atoms and anisotropic thermal parameters for the non-hydrogen atoms, rapidly converged to $R=0.035$. At this point extinction corrections were made according to Zachariasen (1967). Integrated path-lengths were calculated for each reflexion by a Monte-Carlo method, using the same model as for *ABSCOR*. Extinction up to 45% of the measured net intensity was found for the strongest reflexions. The refinement finally resulted in $R=0.0197$ and $R_w=0.0281$. The final positions of the H atoms H(31) and H(41) are somewhat ambiguous. A difference Fourier map calculated without contributions from H revealed broad flat areas of positive electron density in which no precise maximum could be located. The discussion deals with alternative possibilities.

Final positions and thermal parameters are tabulated in Tables 4 and 5.*

Final parameter shifts, except for H(31) and H(41), are < 5% of the estimated standard deviations. A difference Fourier revealed a few peaks above three times the statistical amplitude of $0.13 \text{ e } \text{\AA}^{-3}$. These peaks, with absolute values varying from 0.40 to 0.65 $\text{e } \text{\AA}^{-3}$, were found in the vicinity of the Cu atoms (negative peaks) and of F(2), O(3) and F(4) (positive peaks). The arrangement of peaks around Cu is such that correction by adjusting the temperature parameters or using a different number of electrons is impossible.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31380 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. Fractional coordinates ($\times 10^3$) of H atoms and isotropic thermal parameter B

	x	y	z	B_{iso}
H(11)	111 (4)	-118 (2)	361 (5)	3.5 (4)
H(12)	258 (5)	-15 (3)	486 (6)	5.5 (6)
H(21)	297 (5)	182 (3)	227 (5)	4.8 (5)
H(22)	335 (4)	122 (2)	87 (5)	3.3 (4)
H(31)	361 (5)	386 (3)	43 (5)	4.1 (4)
H(32)	571 (3)	400 (2)	175 (4)	2.0 (3)
H(41)	219 (5)	595 (3)	159 (5)	4.1 (5)
H(42)	146 (4)	610 (2)	291 (5)	3.4 (4)
H(51)	566 (4)	131 (2)	-100 (5)	3.9 (4)
H(52)	407 (4)	184 (2)	-270 (4)	2.4 (3)

Geometry

The two crystallographically independent Cu atoms are octahedrally surrounded by four O atoms and two F atoms. Be is tetrahedrally surrounded by four F atoms. The structure consists of chains of alternating octahedra and tetrahedra along [111] (Fig. 2).

Interatomic distances and angles are listed in Table 6. The average Be-F distance of 1.550 Å is in good agreement with the corresponding value of 1.546 Å in Na₂BeF₄ (Tranqui, Vicat & Aléonard,

Table 6. Interatomic distances (Å) and angles (°)

Distances	
Cu(1)—O(1)	1.966 (2)
Cu(1)—O(2)	1.964 (2)
Cu(1)—F(1)	2.318 (1)
Cu(2)—O(3)	1.949 (1)
Cu(2)—O(4)	1.926 (2)
Cu(2)—F(2)	2.380 (2)
Be—F(1)	1.547 (2)
Be—F(2)	1.548 (1)
Be—F(3)	1.543 (2)
Be—F(4)	1.563 (2)
O(1)—H(11)	0.75
O(1)—H(12)	0.83
O(2)—H(21)	0.73
O(2)—H(22)	0.63
O(3)—H(31)	0.68
O(3)—H(32)	0.73
O(4)—H(41)	0.57
O(4)—H(42)	0.86
O(5)—H(51)	0.75
O(5)—H(52)	0.79
Angles	
O(1)—Cu(1)—O(2)	91.68 (7)
O(1)—Cu(1)—F(1)	89.29 (6)
O(2)—Cu(1)—F(1)	90.54 (5)
F(1)—Be—F(2)	108.9 (1)
F(1)—Be—F(3)	109.3 (1)
F(1)—Be—F(4)	108.1 (1)
H(11)—O(1)—H(12)	107
H(31)—O(3)—H(32)	118
H(51)—O(5)—H(52)	107
O(3)—Cu(2)—O(4)	90.03 (7)
O(3)—Cu(2)—F(2)	87.89 (6)
O(4)—Cu(2)—F(2)	86.88 (5)
F(2)—Be—F(3)	113.2 (1)
F(2)—Be—F(4)	108.0 (1)
F(3)—Be—F(4)	109.2 (1)
H(21)—O(2)—H(22)	115
H(41)—O(4)—H(42)	108

Table 7. Hydrogen bonding: distances (Å) of oxygen-hydrogen, oxygen-acceptor, hydrogen-acceptor; angle (°) oxygen-hydrogen-acceptor; position of the acceptor atom

O	H	A	$d(\text{O-H})$	$d(\text{O-A})$	$d(\text{H-A})$	$\angle(\text{O-H-A})$	Position A*
O(1)	H(11)	F(4)	0.75	2.802	2.11	155	2; 0, 0, 1
O(1)	H(12)	O(5)	0.83	2.777	1.95	177	1; 0, 0, 1
O(2)	H(21)	F(2)	0.73	2.703	2.00	163	1; 0, 0, 0
O(2)	H(22)	O(5)	0.63	2.746	2.13	170	1; 0, 0, 0
O(3)	H(31)	F(4)	0.68	2.702	2.03	174	1; 0, 0, 1
O(3)	H(32)	F(3)	0.73	2.610	1.88	176	1; 1, 0, 0
O(4)	H(41)	F(3)	0.57	2.599	2.03	173	2; 0, 1, 0
O(4)	H(42)	F(4)	0.86	2.648	1.80	168	2; 0, 1, 1
O(5)	H(51)	F(1)	0.75	2.724	2.00	163	1; 1, 0, 0
O(5)	H(52)	F(2)	0.79	2.944	2.17	169	1; 0, 0, 1

* Position of A: symmetry operation ($1 = x, y, z$; $2 = \bar{x}, \bar{y}, \bar{z}$), followed by the translation vector of the unit cell.

1973). The Cu–O and Cu–F distances are about 0.02 and 0.06 Å shorter than the corresponding distances in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The molecular packing of the isomorphous compounds $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{MgCrO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ has been studied extensively by Baur & Rolin (1972). Geometric entities with respect to hydrogen bonding in $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$ are listed in Table 7. The average hydrogen-bond distance (2.725 Å) is about 0.06 Å less than in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, but all interactions are identical with those in copper sulphate.

Discussion

P.m.r. rotation patterns of $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$ showed a doubling of all ten proton signals expected. In addition to possible magnetic explanations of this phenomenon there are three crystallographic possibilities involving slight structural changes in the structure presented, *viz.* (a) doubling of the unit cell, (b) non-centrosymmetric structure, (c) disorder. Weissenberg photographs did not reveal extra reflexions implying a doubling of the unit cell. Reflexion features indicating the presence of an OD structure were not found.

On the other hand there are several atoms in the centrosymmetric structure model with rather high temperature parameters, especially F(2), F(3), O(3) and O(4) (see Table 4). This effect might be due to small deviations from space group $P\bar{1}$. In a first approximation a refinement in space group $P1$ is useful for both cases (b) and (c) as pointed out in the Appendix.

Since cross terms for positions \mathbf{r}_s and $\mathbf{r}_t = -\mathbf{r}_s + \delta$ cumulate systematically in the matrix of normal equations (Srinivasan, 1961) and, moreover, shifts $\Delta\mathbf{r}_s$ and ΔU_{ij_t} of pairs (s, t) are strongly correlated, it was necessary to apply the constraint $U_{ij_s} = U_{ij_t}$ for all nearly centrosymmetric pairs (s, t). H atoms were fixed along calculated directions, using the data of Bacon & Curry (1962), and at distances of 0.75 Å from the O atoms. This geometry of the water molecules was maintained during the refinement. Positional and thermal parameters of the non-centrosymmetric model are listed in Tables 8, 9 and 10. The final discrepancy indices are $R = 0.0196$ and $R_w = 0.0279$. Following Hamilton (1964) we find: $R_w(c)/R_w(ac) = 1.007$ for 3494 observed reflexions and 143 (centrosymmetric model) and 146 (non-centrosymmetric model) parameters. On a 0.005 significance level we find $R_{3,3348,0.005} = 1.002$, in favour of the non-centrosymmetric solution. When comparing the non-centrosymmetric model with a refinement of the centrosymmetric model with fixed H positions, we find an even higher significance level on which the centrosymmetric model can be rejected

$$[R_w(c)/R_w(ac) = 1.047, R_{33,3348,0.005} = 1.009].$$

A comparison of the temperature parameters of the non-centrosymmetric model (Table 9) reveals only

Table 8. Fractional coordinates ($\times 10^4$) of the non-hydrogen atoms of the non-centrosymmetric model

	x	y	z
Cu(1)	0	0	0
Cu(2)	5004 (1)	5001 (1)	5008 (2)
Be	125 (1)	2899 (1)	3874 (2)
*Be'	-127 (1)	-2853 (1)	-3826 (2)
F(1)	-917 (1)	1479 (1)	2367 (2)
F'(1)	1026 (1)	-1450 (1)	-2137 (2)
F(2)	2558 (1)	3209 (1)	4519 (2)
F'(2)	-2576 (1)	-3165 (1)	-4531 (2)
F(3)	-1543 (1)	3803 (1)	2183 (2)
F'(3)	1568 (1)	-3721 (1)	-2026 (2)
F(4)	501 (1)	3045 (1)	6790 (2)
F'(4)	-433 (1)	-2988 (1)	-6711 (2)
O(1)	1810 (1)	-772 (1)	3356 (2)
O'(1)	-1809 (1)	675 (1)	-3466 (2)
O(2)	2863 (1)	1248 (1)	1557 (2)
O'(2)	-2878 (1)	-1151 (1)	-1405 (2)
O(3)	4700 (1)	4118 (1)	1750 (2)
O'(3)	-4629 (1)	-4038 (1)	-1620 (2)
O(4)	2308 (1)	5745 (1)	2481 (2)
O'(4)	-2465 (1)	-5871 (1)	-2688 (2)
O(5)	4382 (1)	1315 (1)	-1764 (2)
O'(5)	-4332 (1)	-1251 (1)	1970 (2)

* Atoms which are added in the non-centrosymmetric space group as opposed to the centrosymmetric space group are indicated with a prime.

Table 9. Anisotropic thermal parameters of the non-hydrogen atoms ($\times 10^4$) of the non-centrosymmetric model

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
Cu(1)	166 (1)	145 (1)	159 (1)	41 (1)	58 (1)	201 (1)
Cu(2)	131 (1)	172 (1)	120 (1)	86 (1)	44 (1)	151 (1)
Be	149 (4)	179 (4)	158 (4)	81 (6)	78 (6)	206 (7)
F(1)	230 (3)	228 (3)	302 (4)	-9 (4)	1 (5)	369 (6)
F(2)	211 (3)	243 (3)	391 (4)	6 (4)	35 (5)	432 (5)
F(3)	284 (3)	360 (3)	289 (3)	357 (5)	371 (6)	386 (5)
F(4)	267 (3)	321 (3)	173 (2)	173 (5)	111 (4)	292 (5)
O(1)	261 (3)	228 (4)	200 (3)	12 (5)	157 (5)	198 (5)
O(2)	226 (3)	177 (4)	242 (3)	-21 (5)	1 (5)	313 (5)
O(3)	175 (3)	436 (5)	169 (3)	71 (6)	134 (6)	207 (6)
O(4)	273 (5)	576 (7)	230 (4)	576 (10)	437 (9)	366 (9)
O(5)	186 (3)	304 (4)	229 (4)	73 (5)	64 (6)	213 (6)

small changes with respect to those of the centrosymmetric model (Table 4). We conclude therefore that the hypothesis that the large temperature parameters indicate a non-centrosymmetric or disordered structure is not justified by the results of the refinement. As has been stated earlier (van Ingen Schenau, Verschoor & Romers, 1974) it is impossible to decide unambiguously between space groups $P1$ and $P\bar{1}$ in cases of minor positional differences between the two alternative structures.

In view of the results of the n.m.r. spectra at about 1 K (Henkens *et al.*, 1975) we suppose that the compound has a large vibrational degree of freedom at room temperature. On cooling, a possible transition towards a non-centrosymmetric structure may account for the observed magnetic behaviour of the crystals. The non-centrosymmetric solution presented here

Table 10. *Calculated fractional coordinates ($\times 10^4$) and thermal parameter B of the H atoms of the non-centrosymmetric model*

	x	y	z	B
H(11)	1150	-1319	3486	3.1 (4)
H'(11)	-1150	1221	-3594	
H(12)	2601	-258	4744	4.4 (5)
H'(12)	-2599	162	-4856	
H(21)	2941	1918	2296	3.2 (4)
H'(21)	-2958	-1822	-2144	
H(22)	3213	1329	577	3.3 (4)
H'(22)	-3227	-1231	-423	
H(31)	3553	3899	264	4.4 (5)
H'(31)	-3487	-3821	-136	
H(32)	5797	4022	1856	2.6 (4)
H'(32)	-5722	-3938	-1724	
H(41)	1911	5867	1037	4.9 (6)
H'(41)	-2069	-5993	-1243	
H(42)	1502	5997	2836	3.3 (4)
H'(42)	-1658	-6123	-3044	
H(51)	5716	1372	-770	4.8 (5)
H'(51)	-5664	-1308	970	
H(52)	4195	1881	-2496	2.4 (4)
H'(52)	-4145	-1819	2704	

might be useful as an indication of the way in which deviations from the centrosymmetric structure could occur.

All calculations were performed on the IBM 370/158 computer of the University of Leiden. Programs were developed in our laboratory, partially based on *ORFLS* (Busing, Martin & Levy, 1962), *ORFFE* (Busing, Martin & Levy, 1964) and *ORTEP* (Johnson, 1965). The authors are indebted to Professor C. Romers for his stimulating interest in this study. This investigation was supported by the Foundation for Investigations by means of X-ray and Electron Diffraction (FOMRE) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

APPENDIX

Starting from the expression for the structure factor in *P* $\bar{1}$

$$F(\mathbf{H}) = 2 \sum f(\cos 2\pi\mathbf{Hr}), \quad (1)$$

with generalized position \mathbf{r} and diffraction vector \mathbf{H} we find the following expressions for the structure factor:

(a) disordered centrosymmetric structure with general positions \mathbf{r} (50%) and $\mathbf{r} + \delta$ (50%) (δ denotes a small displacement vector with respect to position \mathbf{r})

$$F(\mathbf{H}) = \sum f[\cos 2\pi\mathbf{Hr} + \cos 2\pi\mathbf{H}(\mathbf{r} + \delta)]; \quad (2)$$

(b) nearly centrosymmetric structure with positions \mathbf{r} and $-\mathbf{r} - \delta$

$$F(\mathbf{H}) = \sum f[\cos 2\pi\mathbf{Hr} + \cos 2\pi\mathbf{H}(\mathbf{r} + \delta)] + i \sum f(\sin 2\pi\mathbf{Hr} - \sin 2\pi\mathbf{H}(\mathbf{r} + \delta) \cdot \cos 2\pi\mathbf{H}\delta - \cos 2\pi\mathbf{Hr} \cdot \sin 2\pi\mathbf{H}\delta). \quad (3)$$

From the small values for δ and the even and odd character of the cosine and sine functions, it is readily seen that the imaginary part of equation (3) will be negligible, thereby indicating that cases (a) and (b) are indistinguishable.

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