ions are twofold disordered. Such twofold disordering would be among positions satisfying precisely only condition (*a*) above, according to a scheme of the type shown in Fig. 6, or of an analogous type in which in each position one N–O bond coincides with the site $2(x)$ or $2(y)$ axis.

The above critique of the conclusions of Kinoshita *et al.*, permits a simpler and more plausible interpretation than would otherwise be possible of the heat-capacity results obtained by Jewess, Lee-Bechtold & Staveley (1980). These workers observed a heat-capacity anomaly between 37 and 70 K for which the molar anomalous entropy gain was near to $R \ln 2$. No other significant heat-capacity anomalies were observed elsewhere in the entire range 1·5–307 K. The likely significance of these results, then, is that:

(1) between 37 and 70 K, an ordered arrangement of NO_3^- ions passes over into one in which the ions are twofold disordered; and

(2) between 70 and 307 K either (i) this twofold disordering persists, though of course with increasing NO_3^- librational amplitudes, or (ii) the ions tend towards a hindered rotational motion (such a change need not necessarily be sufficiently cooperative to cause a readily observable heat-capacity anomaly).

7. Conclusion

It is suggested that the latter three crystals discussed above are candidates for new structure analyses consistent with the general principles of § 2, and that these principles should be routinely applied for other crystals containing 'orientationally' disordered ions. The extra effort would not be great, involving only the use of simple symmetry arguments to identify those cases where a somewhat larger number of positional parameters needs to be varied than might otherwise be thought necessary. Refinements in such cases should then be less likely to produce self-evidently unsatisfactory positional or vibrational parameters, or to lead to an incorrect determination of the number of positions among which the ions are disordered.

The author is indebted to Dr L. A. K. Staveley of the Inorganic Chemistry Laboratory, Oxford, in whose laboratory he performed his own experiments on two of the four compounds discussed above, and who commented on both drafts of this paper. He also thanks Dr A. K. Cheetham of the Chemical Crystallography Laboratory, Oxford, for commenting on the first draft.

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Electron-Density Distribution and Anharmonic Vibration in Crystals of Potassium Trifluorocuprate(II)

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Abstract

The anharmonic vibration of Cu^{2+} ions in Jahn–Teller-distorted $KCuF_3$ crystals and its effect on electron-density distribution is described. In a previous study [Tanaka, Konishi & Marumo (1979). *Acta Cryst.* B**35**, 1303–1308], the electron-density distribution around the Cu^{2+} ions was analysed assuming mixed

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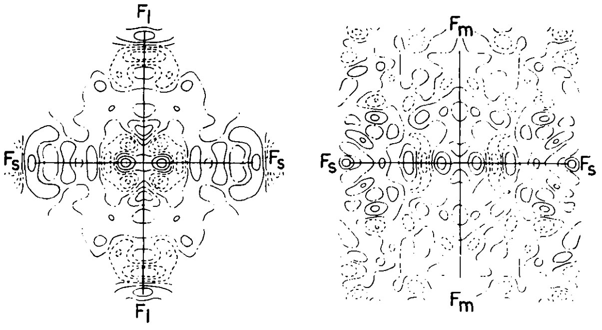
$3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals. The analysis deleted large $3d$ electron peaks on difference Fourier maps. However, it also revealed new significant peaks after the removal of the $3d$ electron peaks. These were ascribed to anharmonic vibration of the Cu^{2+} ions. Anharmonic vibration of the Cu^{2+} ion with point-group symmetry *mmm* was analysed using Willis's method. The calculated one-particle potential has small but significant anharmonicity. The analysis diminished newly revealed peaks on difference Fourier maps, indicating that their origin was the anharmonic vibration of the Cu^{2+} ion. Aspherical peaks on difference Fourier maps of electron-density distribution and of thermal vibration which were supposed to be indivisible were separated in the present study.

Introduction

In previous articles [Tanaka, Konishi & Marumo, 1979 (hereafter referred to as reference *A*), 1980], electron-density distribution in Jahn–Teller-distorted $KCuF_3$ crystals was analysed using five aspherical scattering factors for $3d_{yz}$, $3d_{zx}$, $3d_{xy}$, $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals. The assumption of the Jahn–Teller effect with the wavefunctions in the forms $\Psi_g = \cos(\varphi/2)\,d_{z^2} + \sin(\varphi/2)\,d_{x^2-y^2}$ and $\Psi_e = \sin(\varphi/2)\,d_{z^2} - \cos(\varphi/2)\,d_{x^2-y^2}$, deleted $3d$ electron peaks on the difference Fourier maps. The value of $\cos(\varphi/2)$ was 0·908 (17), which is identical with the value estimated by Kadota, Yamada, Yoneyama & Hirakawa (1967). However, we found a set of peaks lying closer to the central Cu^{2+} ion after the removal of the $3d$ electron peaks as shown in Fig. 1.* In general, aspherical features on an X-ray difference Fourier map consist of asphericities of electron density and atomic vibration. Their separation is considered to be difficult. The purpose of the present article is to examine whether or not the anharmonic vibration is the main cause of the set of peaks in Fig. 1, and to show as a result that the two asphericities are divisible.

Most of the studies on anharmonic vibration have been performed by neutron diffraction; this is because there is no correlation between the two asphericities, and high-index reflexions can be examined more readily (Cooper, Rouse & Willis, 1968). There are, however, several X-ray studies. From powder X-ray intensity measurements, Miyake & Hoshino (1958) observed an anomaly in the Debye–Waller factor of the Cu atom in α-CuI crystals above 673 K. They ascribed this to the anharmonic vibration of the Cu atom following the suggestion by Matsubara (1952, 1975*a*). Recent X-ray studies have been on crystals of Zn (Skelton & Katz, 1968), CaF_2 (Cooper, 1970*a*; Strock & Batterman, 1972), Mg_2Si (Cooper, 1970*b*), Si (Roberto & Batterman, 1970) and Mg_2Sn (Skelton, Lin & Rothberg, 1974). However, these studies were not concerned with electron density, except for that on Si crystals. The present study analyses the electron density and the anharmonic vibration by X-rays, where the asphericity of the electron density was dominant over that of thermal vibration.



(*a*) (*b*)

Fig. 1. The sections of the difference Fourier map before omission of barely significant reflexions calculated with the aspherical scattering factors through the planes determined (*a*) by the $Cu–F_s(u_1)$ and $Cu–F_l(u_2)$ bonds, and (*b*) by the $Cu–F_s(u_1)$ and $Cu–F_m(u_3)$ bonds. Contours are at intervals of 0·2 e $Å^{-3}$. Negative and zero contours are in broken and dashed–dotted lines, respectively.

The point-group symmetry of the Cu^{2+} ion in $KCuF_3$ crystals is *mmm*. Since it is centrosymmetric, the third-order anharmonic terms are impossible and six fourth-order terms are necessary. The third- and fourth-order terms are those which are proportional to the third and fourth powers of the displacement, respectively. Cooper & Rouse (1973) first analysed the anharmonic vibration of Cl^- ions with only the fourth-order terms in KCl crystals. Mair, Barnea, Cooper & Rouse (1974) determined anharmonic fourth-order terms together with the third-order terms in SrF_2 crystals at 773 K. In the present study the six fourth-order terms were calculated in the least-squares refinement.

Theoretical

By employing classical statistics and by assuming a crystal to be a system of independent anharmonic oscillators, an anharmonic temperature factor was formulated by Willis (1969). In the present article, anharmonic vibration of the Cu^{2+} ion was calculated following the method of Willis.

Since the point-group symmetry of the Cu^{2+} ion in crystals of $KCuF_3$ (space group *I4/mcm*) is *mmm*, its vibration at high temperature is described as a motion in an anharmonic potential of the form

$$V(\mathbf{u}) = V_o + \sum_i b_i u_i^2/2 + \sum_{i<j}\sum q_{iijj} u_i^2 u_j^2 + \text{(higher terms)}, \qquad (1)$$

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* This is the corrected version of Fig. 4 of reference *A*.

where $\mathbf{u} = (u_1, u_2, u_3)$ is the displacement vector from the equilibrium position, V_0 is the potential when the atom is at rest and the b_i's and q_{iijj}'s are the harmonic and the fourth-order anharmonic potential parameters, respectively. For the convenience of calculation, u_1, u_2 and u_3 were taken along the directions of the three principal axes of the harmonic thermal ellipsoid – that is, along the Cu—F_s, Cu—F_l and Cu—F_m bonds, respectively (we denote the F atoms at the longest, intermediate and shortest distances from the central Cu^{2+} ion as F_l, F_m and F_s, respectively). Each atom in the crystal is assumed to oscillate independently and the temperature factor, $T(\mathbf{Q})$, of the Cu^{2+} ion for each scattering vector $\mathbf{Q} = 2\pi(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$ in the potential field defined by (1) is calculated as the average by weighting each possible value of $\exp(i\mathbf{Q}.\mathbf{u})$ by its thermodynamic probability (Willis, 1969). $T(\mathbf{Q})$ is derived neglecting higher terms than the fourth,

$$T(\mathbf{Q}) = T^h(\mathbf{Q})[T^c(\mathbf{Q}) + iT^a(\mathbf{Q})], \qquad (2)$$

where $T^h(\mathbf{Q})$ is the harmonic temperature factor and $T^a(\mathbf{Q})$ and $T^c(\mathbf{Q})$ are the terms originating from the third- and fourth-order potential terms, respectively. In the present case,

$$T^h(\mathbf{Q}) = \exp\left(-\sum_i U_i H_i^2/2\right),$$

$$T^c(\mathbf{Q}) = (1 - \xi + \eta - \zeta)/(1 - \xi)$$

and

$$T^a(\mathbf{Q}) = 0,$$

where $U_i = k_B T/b_i$, and k_B and T are Boltzmann's constant and the temperature of the system, respectively. H_i's are defined for each $\mathbf{Q}$ as,

$$\mathbf{Q}.\mathbf{u} = \sum_i u_i H_i.$$

The explicit forms of the H_i's in the present case are

$$H_1 = 2^{1/2}\pi(h + k)\,a^*,$$

$$H_2 = 2^{1/2}\pi(-h + k)\,b^*$$

and

$$H_3 = 2\pi lc^*.$$

If $q_{iijj}/k_B T$ is replaced by Q_{iijj}, ξ, η and ζ are expressed as

$$\xi = \sum_i 3U_i^2 Q_{iiii} + \sum_{i<j}\sum U_i U_j Q_{iijj},$$

$$\eta = \sum_i 6H_i^2 U_i^3 Q_{iiii} + \sum_{i<j}\sum (H_i^2 U_i + H_j^2 U_j)\, U_i U_j Q_{iijj}$$

and

$$\zeta = \sum_i H_i^4 U_i^4 Q_{iiii} + \sum_{i<j}\sum H_i^2 H_j^2 U_i^2 U_j^2 Q_{iijj}.$$

ξ, η and ζ are the terms proportional to $k_B T$, $(k_B T)^2$ and $(k_B T)^3$, respectively. The details of this procedure will be presented elsewhere (Tanaka & Marumo, 1982).

Analysis of the thermal motion

The peaks around the Cu^{2+} ion in Fig. 1 were ascribed to the anharmonic vibration of the Cu^{2+} ion and an incomplete approximation of the electron-configuration model in reference *A*. Thermal vibration has a larger effect on higher-angle reflexions, while the effect of the diffuse outer-shell electron is minor in these reflexions. The series-termination effect becomes smaller if higher-angle reflexions are included in the calculation. Thus the refinement was performed for the four data sets with $\sin\theta/\lambda$ less than 0·6, 1·0, 1·31 ($2\theta < 137°$) and 1·37 $Å^{-1}$ ($2\theta < 153°$), respectively, to which we refer hereafter as DATA 1, DATA 2, DATA 3 and DATA 4, respectively. DATA 3 were used in reference *A*. A preliminary calculation with DATA 3 revealed only slight differences between harmonic and anharmonic structure factors which were not more than twice the statistical counting error. Thus we omitted the barely significant reflexions whose crystallographically equivalent reflexions had no significant structure factors. Structure factors of all the reflexions omitted were less than five times their statistical counting error. The number of those extracted from DATA's 1, 2, 3 and 4 were 1, 25, 71 and 71, respectively.

Refinements were first performed following the method in reference *A*. The atomic parameters and *R* factors, defined as $R_1 = \sum \left||F_o| - |F_c|\right| / \sum |F_o|$ and $R_2 = [\sum (|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$, are listed in Table 1. R_1' and R_2' in the table are R_1 and R_2 values after equivalent reflexions were averaged. We then introduced anharmonic terms into our least-squares program *LINKT*79 written by one of the authors (KT). Using DATA's 2, 3* and 4, the anharmonic vibration of the Cu^{2+} ion was analysed. Starting from zero, the anharmonic parameters Q_{iijj} were refined fixing all the other parameters. The Q_{iijj}'s were transformed to q_{iijj}'s in equation (1) taking the temperature of the system as 296 K; these are listed in Table 2 together with the b_i's and the *R* factors. All the parameters were then refined at the same time. However, the refinement diverged because of severe correlation between harmonic and anharmonic temperature factors along the same direction – that is, between U_{11} and Q_{1122}, U_{33} and Q_{3333}, U_{12} and Q_{1111}, U_{12} and Q_{2222}. Such severe correlation was also reported by Cooper & Rouse (1973) and by Mair, Barnea, Cooper & Rouse (1974). In Table 2, *n* is the number of structure factors whose deviations from those calculated with the harmonic model were greater than their estimated standard deviations based on the counting statistics. The small values of *n* as well as a slight improvement of the *R* factors indicate the lesser

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* A list of structure factors for DATA 3 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36577 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* (×10^5), *anisotropic temperature factors* (×10^5 Å^{-2}), *anisotropic type* I *extinction parameters* (×10^3) *and the coefficient* cos ($\varphi/2$) (×10^3)

The form of the temperature factor is defined as exp $\{-2\pi^2[(h^2 + k^2)a^{*2}U_{11} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12}]\}$. Values in parentheses are the e.s.d.'s.

	DATA 1 (sin $\theta/\lambda \le$ 0·6 Å^{-1})	DATA 2 (sin $\theta/\lambda \le$ 1·0 Å^{-1})	DATA 3 (sin $\theta/\lambda \le$ 1·31 Å^{-1})	DATA 4 (sin $\theta/\lambda \le$ 1·37 Å^{-1})
Cu U_{11}	735 (24)	761 (6)	760 (3)	767 (3)
U_{33}	603 (25)	580 (8)	574 (3)	579 (3)
U_{12}	−116 (15)	−111 (6)	−116 (4)	−116 (4)
K U_{11}	1568 (30)	1545 (7)	1543 (5)	1548 (5)
U_{33}	1469 (40)	1460 (10)	1446 (6)	1448 (6)
F(1) U_{11}	2155 (70)	2224 (22)	2231 (17)	2232 (17)
U_{33}	747 (92)	708 (24)	719 (14)	726 (14)
F(2) x	22726 (15)	22755 (7)	22758 (6)	22757 (6)
U_{11}	1313 (46)	1358 (14)	1367 (11)	1375 (11)
U_{33}	2055 (72)	2016 (25)	1989 (19)	1994 (19)
U_{12}	−708 (54)	−638 (20)	−616 (14)	−613 (14)
cos ($\varphi/2$)	923 (44)	900 (24)	902 (16)	898 (16)
G_{11}	96 (6)	99 (4)	98 (3)	99 (3)
G_{22}	158 (7)	159 (5)	158 (5)	160 (5)
G_{33}	339 (49)	357 (35)	355 (31)	364 (32)
G_{12}	84 (3)	86 (2)	84 (2)	85 (2)
G_{13}	−68 (12)	−65 (8)	−65 (8)	−65 (8)
G_{23}	−6 (22)	1 (16)	−3 (14)	−2 (15)
R_1	0·0068	0·0085	0·0105	0·0112
R_2	0·0070	0·0083	0·0100	0·0104
Number of reflexions	125	468	888	953
R_1^I	0·0052	0·0066	0·0084	0·0093
R_2^I	0·0057	0·0067	0·0079	0·0084
Number of independent reflexions	72	263	500	541

Table 2. *Harmonic* (×10^{-19} J Å^{-2}) *and anharmonic* (×10^{-19} J Å^{-4}) *potential parameters at* 296 K

Values in parentheses are the e.s.d.'s.

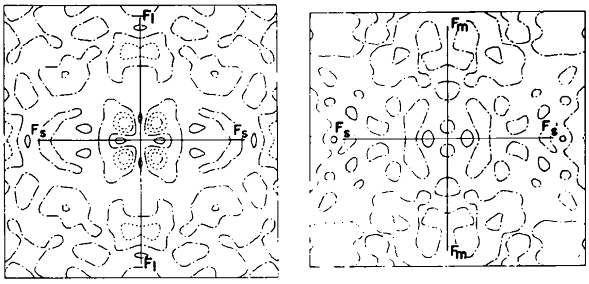
	DATA 2	DATA 3	DATA 4
b_1	6·29 (0·05)	6·34 (0·04)	6·28 (0·03)
b_2	4·69 (0·03)	4·67 (0·02)	4·63 (0·02)
b_3	7·05 (0·09)	7·13 (0·04)	7·06 (0·04)
q_{1111}	−8·3 (6·3)	−5·6 (3·6)	−5·0 (3·4)
q_{2222}	−4·4 (2·8)	−2·3 (1·6)	−1·6 (1·5)
q_{3333}	2·9 (5·2)	1·2 (2·1)	0·4 (1·9)
q_{1122}	42·3 (10·2)	24·3 (4·2)	18·8 (3·9)
q_{1133}	−5·5 (39·4)	1·4 (22·4)	4·5 (21·6)
q_{2233}	−8·0 (23·4)	−5·2 (13·4)	−5·2 (13·1)
R_1	0·0082	0·0101	0·0109
R_2	0·0082	0·0097	0·0102
n	13	19	14
R_1^I	0·0064	0·0079	0·0088
R_2^I	0·0065	0·0076	0·0082

importance of the anharmonicity in the present crystal at room temperature.

Results and discussion

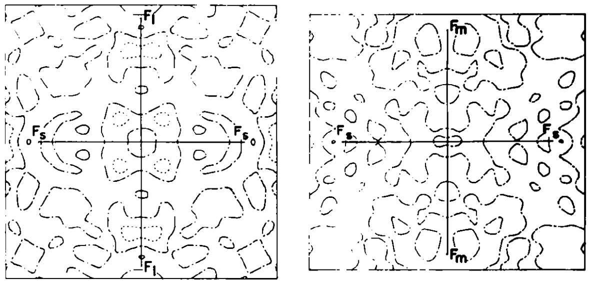
Since the analysis did not change the positional parameters significantly, the Cu–F bond lengths are the same as those obtained in reference *A*. All the analyses improved the *R* factors slightly as shown in Tables 1 and 2.

The analysis of DATA 3 with the harmonic model gave the residual densities shown in Fig. 2. The analysis of DATA 1 (sin θ/λ < 0·6 Å^{-1}) exhibits no peak greater than 0·1 e Å^{-3}. The negative peaks around the Cu^{2+} ion in the maps of DATA's 2 to 4 have heights of −0·32, −0·57 and −0·65 e Å^{-3}, respectively. The heights of the positive peaks on the Cu–F$_s$ bonds are 0·04, 0·30 and 0·29 e Å^{-3} and those on the Cu–F$_l$ bonds are 0·18, 0·26 and 0·23 e Å^{-3}, respectively. These peaks have a tendency to become more prominent as the higher-angle reflexions are included in the calculation. Also, most of the 3*d* electron peaks had already been removed by the refinement with aspherical scattering factors. Thus the remaining peaks may be ascribed to the anharmonic vibration of the Cu^{2+} ion. They were hidden by the dominant 3*d* electron peaks in Fig. 2 of reference *A*. In fact, they began to be revealed more explicitly as the more exact electron-configuration models were employed as seen in Figs. 3 and 4 of reference *A*.



(*a*) (*b*)

Fig. 2. The sections of the difference Fourier map using the reflexions with sin θ/λ less than 1·31 Å^{-1} through the same planes as in Fig. 1. Contours are at intervals of 0·2 e Å^{-3}. Negative and zero contours are in broken and dashed–dotted lines, respectively.



(*a*) (*b*)

Fig. 3. The sections of the difference Fourier map after the refinement with DATA 3 with anharmonic vibration assumed for the Cu^{2+} ion, through the same planes as in Fig. 1. Contours are at intervals of 0·2 e Å^{-3}. Negative and zero contours are in broken and dashed–dotted lines, respectively.

The difference Fourier map after the refinement with DATA 3 assuming anharmonic vibration of the Cu^{2+} ion is shown in Fig. 3. The positive peaks on the Cu–F_s and Cu–F_l bonds have disappeared and the negative peaks are reduced from $-0{\cdot}57$ to $-0{\cdot}28$ e $Å^{-3}$, moving about 0·07 Å away from the Cu^{2+} ion. Accordingly, we attribute the peaks around the Cu^{2+} ion in Fig. 2 to the anharmonic vibration of the Cu^{2+} ion. Separation on difference Fourier maps of the peaks due to aspherical electron distribution from those due to thermal motion has been supposed to be difficult. However, anharmonic-vibration peaks which were hidden by the dominant 3*d* electron peaks were revealed after the removal of the 3*d* electron peaks. The present study, we believe, is the first case of a successful division of the two asphericities. This also promises a more exact anharmonic-vibration study by X-rays.

The tops of the anharmonic-vibration peaks lie closer to the central Cu^{2+} ion than those due to 3*d* electron distribution. In order to estimate the anharmonicity of the Ni atoms in γ-Ni_2SiO_4 crystals, Isobe & Marumo (1975) calculated structure factors F_c^s's assuming split Ni atoms distributed along the body diagonals of the unit cell. Evaluating the Fourier transform of $(F_c^s - F_c)$'s, they found the peaks to lie closer to the Ni atom than those obtained in the usual difference Fourier map.

The anharmonic potential parameters in Table 2 explain well the difference Fourier maps in Fig. 2. The large positive q_{1122} makes the Cu^{2+} ion vibrate such that it avoids the direction bisecting the Cu–F_s and Cu–F_l bonds and, in fact, the large negative peaks in Fig. 2 appeared along this direction. Two negative values for q_{1111} and q_{2222} indicate the preferential vibration of the Cu^{2+} ion along the Cu–F_s and Cu–F_l bonds, resulting in positive peaks on these bonds. The non-significance of the remaining anharmonic potential parameters corresponds to the fact that no significant peaks were found near the Cu^{2+} ion except on the plane $u_3 = 0$. The anharmonic fourth-order potential V_q on the plane $u_3 = 0$,

$$(V_q)_{u_3=0} = q_{1111}\,u_1^4 + q_{2222}\,u_1^4 + q_{1122}\,u_1^2\,u_2^2,$$

is depicted in Fig. 4, taking the q_{iijj}'s from the refinement of DATA 3. As described in the preceding discussion, negative and positive peaks in Fig. 2 appear where the potential in Fig. 4 is positive and negative, respectively. The potential is at a minimum along the Cu–F_s ($u_1 = 0$) and Cu–F_l ($u_2 = 0$) bonds and is at a maximum when $u_2 = \pm(q_{1111}/q_{2222})^{1/4}u_1$ or $u_2 = \pm(1{\cdot}25 \pm 0{\cdot}19)u_1$. V_q becomes zero on the lines $u_2 = \pm 0{\cdot}485u_1$ and $u_2 = \pm 3{\cdot}21u_1$. The potential shows that the attractive Coulombic forces between Cu^{2+} and F^- ions have greater influence on the anharmonic vibration than do the repulsive forces between atomic cores. This was also pointed out by Cooper & Rouse (1976) in KCl crystals.

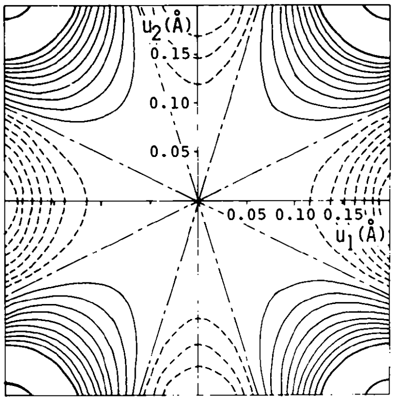


Fig. 4. The section of the anharmonic potential of the Cu^{2+} ion through the same plane as in Fig. 1(*a*). Contours in thin and thick lines are at intervals of 10^{-22} and 10^{-21} J, respectively. Negative contours are in broken lines and at intervals of 10^{-22} J. Zero contours are in dashed–dotted lines.

Following Willis (1969), power-series expansion of $\exp(-V_q/k_BT)$ terminated at the term $(-V_q/k_BT)$, and the higher-order terms were neglected. Matsubara (1975*b*) pointed out that power-series expansion is always divergent because of the unbounded nature of the potential (1). The root-mean-square displacements (r.m.s.d.'s) of the Cu^{2+} ion are 0·080, 0·094 and 0·076 Å along the u_1, u_2 and u_3 axes, respectively. V_q/k_BT at the r.m.s.d.'s are 6·41, 4·36 and $6{\cdot}68 \times 10^{-3}$ along the u_1, u_2 and u_3 axes, respectively. Thus Willis's treatment is justified quite well in the present case.

No correction was made for thermal diffuse scattering (TDS). Intensity addition to the net intensity by TDS reduces temperature factors. Since most of the U_{ij}'s in Table 1 increase slightly from DATA 3 to DATA 4, TDS may not have a significant effect in the present case. However, the slight decrease of the positive difference Fourier peaks along the Cu–F_l and Cu–F_s bonds from DATA's 3 to 4 might be due to the TDS effect. Thus TDS could not be neglected in the more accurate analysis of thermal motion or in the analysis at higher temperature.

Omission of unreliable reflexions resulted in difference Fourier maps with low noise level, though Figs. 1 and 2 showed approximately the same features. The parameter $\cos(\varphi/2)$ of the Cu^{2+} ion shifted only slightly within the standard deviation from 0·908 (17) to 0·902 (16) by omitting reflexions.

The negative peaks around the Cu^{2+} ion which are the largest in Fig. 3 might be due to the core deformation density (Bentley & Stewart, 1974) and/or insufficient approximation of the electron-configuration model. Yamatera (1979) proposed that the tetragonal elongation of octahedral copper(II) complexes distorted by the Jahn–Teller effect should be interpreted by considering interactions with the lowest excited state, with an electron excited to the 4*s* orbital. In the present study, we did not consider 4*s* electrons and non-localized electrons of the metal and ligand atoms.

For further study of the anharmonic-vibration effect in $KCuF_3$ crystals by X-ray diffraction, it is necessary to measure intensities at higher temperature where anharmonic motion is expected to become larger and the peaks on the difference Fourier map due to the anharmonic vibration become prominent.

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Structure du Nitrurotrioxoosmate(VIII) de Césium, $CsOsO_3N$; Comparaison avec $BaSO_4$

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Abstract

$CsOsO_3N$ is orthorhombic, space group *Pnma*, with $a = 8\cdot409\ (1)$, $b = 7\cdot242\ (1)$, $c = 8\cdot089\ (1)$ Å, $Z = 4$, $V = 492\cdot6\ (2)$ Å^3, $d_x = 5\cdot19$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 34\cdot8$ mm^{-1}. The structure was refined to $R = 0\cdot043$ for 561 unique reflexions. It consists of isolated $[OsO_3N]$ tetrahedra linked together by Cs^+ ions. The packing is related to the $BaSO_4$-type structure. The ordered arrangement between O and N atoms leads to quite different axial ratios with respect to the $BaSO_4$-type compounds. The coordination of the Cs^+ ions has been found to be 10 according to the 'effective coordination number' method.

I. Introduction

Des travaux antérieurs ont permis de préparer et de déterminer la structure de composés de formule M^IOsO_3N. Lorsque M^I est le potassium, la structure est de type scheelite $CaWO_4$ (Laurent, Pastuszak, L'Haridon & Marchand, 1982); elle est de type

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