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ESR Study of Cr^{3+} and Fe^{3+} Ions in $KGaF_4$ Single Crystals

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$KGaF_4$ (*Pnma*, a = 12.211(7) Å, b = 7.496(2) Å, c = 7.635(3) Å, Z = 8) accurate X-ray structure determination has been carried out from 1754 reflections at room temperature (R = 0.0256, R_w = 0.0312). An accurate determination of spin Hamiltonian parameters for Cr^{3+} and Fe^{3+} ions in this host compound has been achieved. Intrinsic superposition model parameters are deduced and the validity of the model is discussed in this low-symmetry case. A structural phase transition occurring at about 465 K has been detected.

Introduction

The present paper is a contribution to a more general work about the correlations between spin Hamiltonian parameters of a 3*d* ion (Cr^{3+}, Fe^{3+}) in an octahedral ligand field and the host matrix crystal structure.

The empirical superposition model (SPM) (*1*) which assumes that the spin Hamiltonian parameters result from individual contributions of each nearest neighbor of the paramagnetic ion has been used frequently. In a first step the SPM has been used with some success for high-symmetry host lattices and later for some low-symmetry cases such as $Na_5Al_3F_{14}$ (*2*), $Cs_2NaAl_3F_{12}$ (*3*), and the tetrafluoaluminates $AAlF_4$ (A = K, Rb, NH_4) (*4, 5*). For all these crystals, the discrepancy between the ionic radii of Cr^{3+} or Fe^{3+} and Al^{3+} may induce distortions of the fluorine octahedron.

This consideration has oriented our attention to gallium compounds. Unfortunately the growth of single crystals of tetrafluogallates is not trivial and actually only $KGaF_4$ is available.

Structure of $KGaF_4$

Preparation

Owing to the previous results of J. Chassaing (*6*), the synthesis of the low-temperature form of $KGaF_4$ was done at a temperature below 530°C. Single crystals could be grown by using a chloride flux technique described elsewhere (*7, 8*). The best results were obtained from a flux of composition

$$2KF + 2GaF_3 + 6KCl + 6ZnCl_2 \rightarrow (2KGaF_4 + 6KCl + 6ZnCl_2)$$

by slow cooling (5°C/hr) from 500°C. The crystals, forming rectangular platelets of dimension up to 5 mm are lightly sensitive to moisture.

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TABLE I

CONDITIONS OF THE DATA COLLECTION OF $KGaF_4$ (L.T.) ON SIEMENS-AED2 (Mo$K\alpha$)

a = 12.211(7) Å, b = 7.496(2) Å, c = 7.635(3) Å
V = 698.86 Å^3, Z = 8
dR_x = 3.51 g/cm^3
Crystal volume: 1.08 × 10^{-2} mm^3
Scanning mode: $\omega/2\theta$, Aperture: D = 4.0 mm
Angular range: 3° ≤ 2θ ≤ 90°
hkl max: 24, 14, 15
Absorption coefficient μ(cm^{-1}): 89.81
Transmission factor (min, max): 0.18, 0.41
Reflections measured (total, independent): 3483, 2504
Reflections used in refinement ($\sigma(I)/I$ < 0,33): 1754
Maximum height in Fourier difference map: 0.12e^-/Å^3

For ESR experiments, chromium chloride or iron fluoride was added to the growth mixture in amounts corresponding to a molar ratio M^{3+}/Ga^{3+} = 0.01 and 0.02, respectively.

Structure Determination

The results of the crystallographic study—Laüe symmetry *mmm*; limiting conditions for reflections $0kl$: $k + l = 2n$, $hk0$: $h = 2n$, $h00$: $h = 2n$, $0k0$: $k = 2n$, and $00l$: $l = 2n$—are consistent with the *Pnma* space group (N° 62) and the noncentric $Pn2_1a$ space group (N° 33). The X-ray powder diffraction spectrum of crushed crystals is well indexed with the cell parameters a = 12.21 Å, b = 7.49 Å, and c = 7.64 Å. A crystal of approximate size (0.3 × 0.1 × 0.3) mm^3 was chosen for the structure determination. The cell parameters were refined from 24 reflections well distributed in the reciprocal space. Because of the large volume of the crystal, absorption correction was applied. Table I gathers the conditions of the diffraction experiment on AED2 diffractometer. All the calculations were made with the SHELX76 program (*9*). Atomic scattering factors and anomalous dispersion values were taken from "International Tables for X-Ray Crystallography" (*10*).

In the *Pnma* space group, the Ga and K positions were deduced from a Patterson map and for the fluorines by analogy with the $KFeF_4$ phase III model (*13*). With these positions and isotropic thermal motion for all the atoms, the R and R_w factors were 0.080 and 0.089, respectively. By refining the anisotropic thermal parameters the R and R_w values fall to 0.0256 and 0.0312, respectively, with a weighting scheme w =

TABLE II

STRUCTURAL PARAMETERS OF $KGaF_4$
U_{ij} VALUES ARE ×10^4 (ESD'S IN PARENTHESES)

Atom	Site	x	y	z	B_{eq} (Å^2)	U_{11}[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ga	8d	0.2491(0)	0.0004(0)	0.1249(0)	0.57	100(1)	51(1)	66(1)	1(0)	1(0)	−4(0)
K_1	4c	0.5180(0)	3/4	0.1237(1)	1.37	224(2)	134(2)	161(2)	0	−3(3)	0
K_2	4c	0.9747(0)	1/4	0.1242(1)	1.38	222(2)	141(2)	163(2)	0	0(3)	0
F_1	8d	0.7520(1)	0.0358(2)	0.1246(2)	1.63	360(7)	186(5)	72(4)	−4(5)	−2(3)	21(4)
F_2	4c	0.2805(1)	3/4	0.1580(2)	1.23	211(6)	60(5)	197(6)	0	−31(5)	0
F_3	4c	0.2167(1)	1/4	0.0924(2)	1.22	208(6)	57(5)	198(7)	0	−23(5)	0
F_4	8d	0.1024(1)	−0.0426(1)	0.1284(2)	1.33	110(3)	146(4)	250(4)	−12(6)	5(5)	−17(3)
F_5	8d	0.3957(1)	0.0437(1)	0.1163(2)	1.22	111(3)	143(4)	209(4)	19(5)	5(4)	−20(3)

[a] The vibrational coefficients are relative to the expression $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2kl\, b^*c^*U_{23} + 2hl\, a^*c^*U_{13} + 2hk\, a^*b^*U_{12})]$.

$1.0/(\sigma^2(F) + O(F)^2)$ and a secondary extinction factor $x = 3.40 \times 10^{-7}$. Attempts to refine this structure in the noncentric $Pn2_1a$ space group did not lead to a lower R factor. Table II gives the best set of atomic coordinates and the thermal motion parameters in *Pnma*. Observed and calculated structure factors can be obtained upon request to the authors (G.C.)

Structure Description

The $KGaF_4$ structure, shown in Fig. 1, is derived from the $TlAlF_4$ aristotype (*11, 12*) by both rotations of octahedra and shift of sheets. It is isotypic with the $KFeF_4$ structure (phase III) (*13*). It can be described as two GaF_4^- octahedra sheets perpendicular to the [100] direction and located in the vicinity of levels $x = 1/4$ and 3/4. Two consecutive sheets are shifted from each other by $c/4$. In the nearly regular GaF_6^{3-} octahedron (Table III) two kinds of Ga–F distances are observed: four equatorial distances of about 1.928 Å (two with F_1 atoms, two with F_2 and F_3 atoms) and two shorter axial distances of about 1.820 Å. These results are in good agreement with those observed for similar structures such as $KFeF_4$ (*13*) or NH_4FeF_4 (*14*). The octahedra rotation is the same from one sheet to another. According to the Glazer notation (*15*) the tilting mode shall be described as $a^+b_p^+c_p^+$ if we consider that the sheet at $x = 3/4$ is shifted from $-c/4$ (see Fig. 2). The K^+ ions are located in holes limited by four terminal fluorines coming from one sheet and two other terminal fluorines coming from another shifted sheet. According to the tilting mode in the (b, c) plane two different sites are observed for the potassium ions.

ESR Measurements

When using regular conventions of crystallography the space group of $KGaF_4$ is therefore *Pnma*. For ESR interpretation it is more convenient to work in a frame where the c axis is perpendicular to the GaF_4 layers.

Subsequently, we consider now for $KGaF_4$ a unit cell where a = 7.496 Å, b =

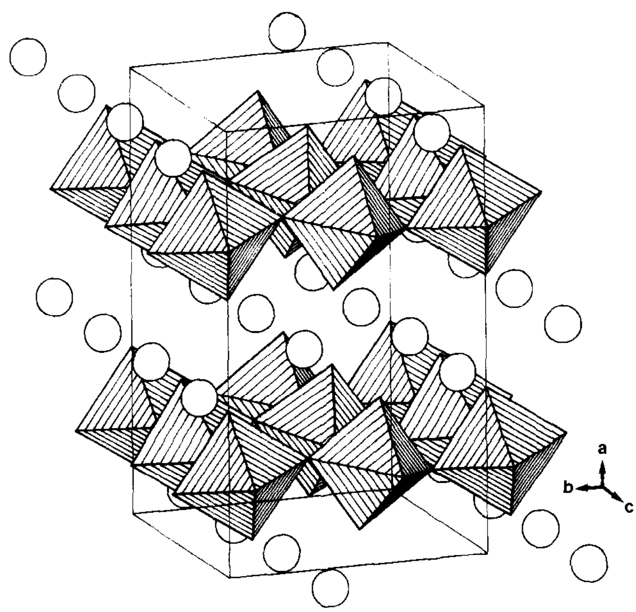

FIG. 1. Perspective view of $KGaF_4$ structure drawn by means of the STRUPLO84 program (*15*).

TABLE III

MAIN INTERATOMIC DISTANCE (Å) AND BOND ANGLES (°) IN $KGaF_4$ (ESD'S ARE GIVEN IN PARENTHESES)

$Ga-F_1$ = 1.924(1)	F_1-F_2 = 2.719(2)	F_1-Ga-F_1' = 179.3(2)
$Ga-F_1'$ = 1.931(1)	F_1-F_3 = 2.733(2)	F_1-Ga-F_3 = 90.5(1)
$Ga-F_2$ = 1.931(0)	F_1-F_4 = 2.625(1)	F_3-Ga-F_1' = 89.9(1)
$Ga-F_3$ = 1.927(0)	F_1-F_5 = 2.644(2)	F_1-Ga-F_2 = 89.6(1)
$Ga-F_4$ = 1.820(1)	$F_1'-F_2$ = 2.733(2)	F_2-Ga-F_1' = 90.0(1)
$Ga-F_5$ = 1.820(1)	$F_1'-F_3$ = 2.725(2)	F_3-Ga-F_2 = 179.6(2)
$\langle Ga-F_{eq}\rangle$ = 1.928	$F_1'-F_4$ = 2.651(1)	F_1-Ga-F_4 = 89.0(1)
$\langle Ga-F_{ax}\rangle$ = 1.820	$F_1'-F_5$ = 2.643(1)	F_1-Ga-F_5 = 89.8(1)
$\langle Ga-F\rangle$ = 1.892	F_2-F_4 = 2.684(2)	$F_1'-Ga-F_4$ = 91.6(1)
Ga-F theo = 1.905	F_2-F_5 = 2.631(1)	$F_1'-Ga-F_5$ = 89.6(1)
	F_3-F_4 = 2.613(1)	F_3-Ga-F_4 = 88.4(1)
	F_3-F_5 = 2.631(1)	F_3-Ga-F_5 = 91.3(1)
		F_2-Ga-F_4 = 91.3(1)
		F_2-Ga-F_5 = 89.0(1)
		F_4-Ga-F_5 = 178.8(2)
2× K_1-F_4 = 2.657(2)		
2× K_1-F_5 = 2.659(2)	$\langle K_1-F\rangle$ = 2.645	
2× K_1-F_5 = 2.619(2)		
2× K_2-F_4 = 2.690(2)		
2× K_2-F_4 = 2.649(2)	$\langle K_2-F\rangle$ = 2.677	
2× K_2-F_5 = 2.692(2)		

7.635 Å, and c = 12.211 Å ($Pmcn$ space group). ESR studies are done on a conventional X band (3 cm) spectrometer. The use of a two perpendicular axes goniometer allows fine orientations of crystal in the magnetic field. The ESR analysis shows unambiguously that Cr^{3+} ion or Fe^{3+} ion is substituted for the Ga^{3+} ion: The local symmetry is 1 (8d site).

The ESR spectra have been fitted to the following spin Hamiltonian:

$$\mathcal{H} = \mu_B HgS + 1/3(b_2^0O_2^0 + b_2^1O_2^1 + b_2^2O_2^2) + 1/64\left(\sum_{i=0}^{4} b_4^iO_4^i\right)$$

(for Cr^{3+} ion, the fourth-order parameters are not present).

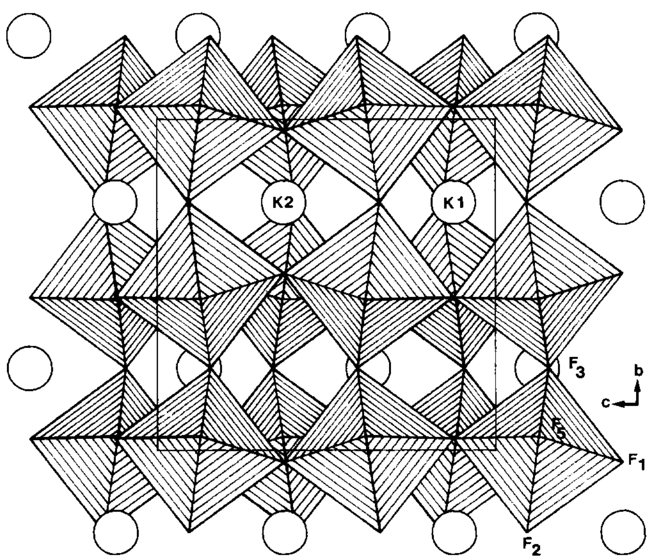

FIG. 2. The (100) projection of $KGaF_4$ structure. (Only K^+ ions at x = 1/2 are evidenced.)

The Steven's operators O_n^m are expressed in a reference frame (x_n^m, y_n^m, z) in which all b_n^{-m} vanish. The z axis is [001], and the x_n^m axes are defined by the a_n^m angles between [100] and x_n^m.

The spin Hamiltonian parameters determination is not trivial. The multiplicity of the sites in the cell unit, the superhyperfine interaction (Fe^{3+} case), and the fine structure transitions which do not obey the normal selection rules give knotty spectra (Fig. 3). All parameters were determined by using a computer program. The complexity of the superhyperfine structure prevents precise determination of the fourth-order parameters for the Fe^{3+} ion.

The set of spin Hamiltonian parameters which gives the best agreement between calculated and experimental ESR lines positions is registered in Table IV. These values account for any details of the experimental spectra accurately.

TABLE IV

SPIN HAMILTONIAN PARAMETERS FOR $KGaF_4:Cr^{3+}$ AND FOR $KGaF_4:Fe^{3+}$

Cr^{3+}	
$gz = 1.97(5)$,	$gx = gy = 1.98(5)$
$b_2^0 = -1585 \pm 20\ 10^{-4}$ cm^{-1}	
$b_2^1 = -3270 \pm 20\ 10^{-4}$ cm^{-1},	$a_2^1 = \pm 64° \pm 2°$
$b_2^2 = 580 \pm 20\ 10^{-4}$ cm^{-1},	$a_2^2 = \pm 17° \pm 2°$
Fe^{3+}	
$gz = 2.002(3)$,	$gx = gy = 2.003(5)$
$b_2^0 = 1526 \pm 20\ 10^{-4}$ cm^{-1}	
$b_2^1 = 2060 \pm 20\ 10^{-4}$ cm^{-1},	$a_2^1 = 2° \pm 0.5°$
$b_2^2 = 470 \pm 20\ 10^{-4}$ cm^{-1},	$a_2^2 = 10° \pm 1°$
$b_4^0 = -25 \pm 20\ 10^{-4}$ cm^{-1}	

Discussion of the SPM

The superposition model has been introduced by Newman (*1*). It supposes that the spin Hamiltonian parameters depend only on the local surrounding of the paramagnetic ion through the law

$$b_n^m = \sum \bar{b}_n(R_i)\ K_n^m(\theta_i, \Phi_i),$$

where i runs over the nearest neighbors at coordinates R_i, θ_i, and Φ_i.

—$\bar{b}_n(R_i)$ is an intrinsic radial function and

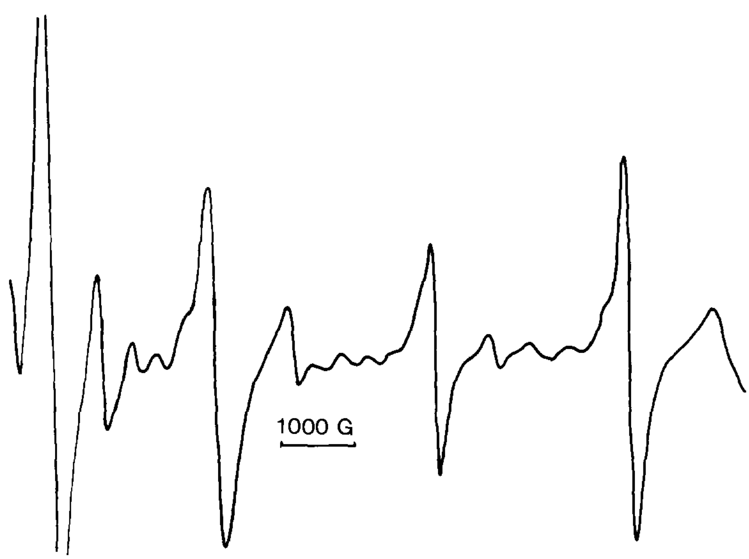

FIG. 3. ESR spectrum of $KGaF_4:Fe^{3+}$. Magnetic field along [001]. Central field is 5000 G and sweep is 10,000 G.

it is generally assumed that it obeys an exponent law

$$\bar{b}_n(R_i) = b_n(R_0) \cdot (R_0/R_i)^{t_n},$$

where R_0 is a reference length and t_n an adjustable parameter.

—The $K_n^m(\theta_i, \Phi_i)$ are angular functions similar to the spherical harmonics. The relevant functions for this work are:

$$K_2^0 = 1/2(3 \cos^2 \theta - 1)$$

$$K_2^1 = 3 \cdot \sin 2\theta \cdot \cos \Phi, \quad K_2^{-1} = 3 \cdot \sin 2\theta \cdot \sin \Phi$$

$$K_2^2 = 3/2 \sin^2 \theta \cdot \cos 2\Phi, \quad K_2^{-2} = 3/2 \sin^2 \theta \cdot \sin 2\Phi.$$

A rigorous calculation taking account of the geometry of the octahedron (Fig. 4) and using for R the average Ga–F bond length has been undertaken with the help of a computer program. The best fits between the calculated and the experimental values are summarized in Table V.

Fe^{3+}. Except for the b_2^2 value the agreement is good. The t_2 value is comparable to the value t_2 = 10 obtained in $Na_5Al_3F_{14}$ (*2*) and the value t_2 = 7 used for $Cs_2NaAl_3F_{12}$ (*3*). In the field of the SPM, for high values of t_2 the difference between the bond lengths is the most important contribution arising in Hamiltonian parameters calculations.

Cr^{3+}. It is not possible to obtain simultaneously a correct agreement with the b_2^0 and the b_2^1 values. In this case the low value of t_2 shows that the angular distortion is determinant in the calculations of Hamiltonian parameters.

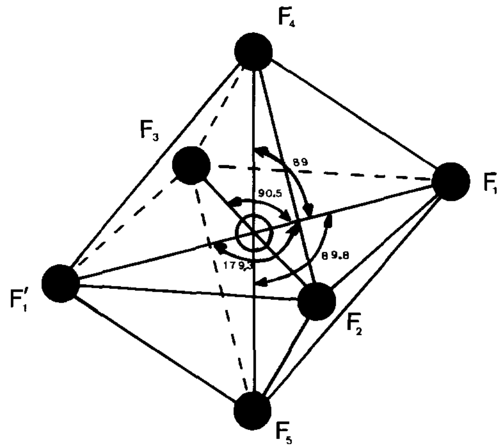

FIG. 4. The GaF_6^{3-} octahedron in $KGaF_4$ with some angular values (in degrees).

For $KGaF_4$ the lengths of the Ga–F bonds are very different for equatorial bonds (R = 1.928 Å) and for axial bonds (R = 1.820 Å). A large variation of the $\bar{b}_2(R)$ value in the vicinity of these R values may account for the discrepancy between experimental and calculated values. So in a second step we have made SPM calculations in using different values of b_2 and t_2 for the two kinds of bonds. With the help of a computer program we have also studied the effect of a possible lattice relaxation around the impurity. For this study the R_i values are unaltered and for θ_i and Φ_i the deviations are limited to ±1.5° amplitude.

The best fits are summarized in Tables VI and VII. Apart from b_2^2 (Fe^{3+}) the agreement is very good. For Fe^{3+} the assumption of a large variation of $\bar{b}_2(R)$ with R seems to be confirmed.

TABLE V

DIRECT APPLICATION OF THE SPM TO $KGaF_4:Cr^{3+}$ AND TO $KGaF_4:Fe^{3+}$

	$b_2(R)$ 10^{-4} cm^{-1}	t_2	b_2^0 (10^{-4} cm^{-1})	b_2^1 (10^{-4} cm^{-1})	a_2^1	b_2^2 (10^{-4} cm^{-1})	a_2^2
Cr^{3+}	−9800	1.2	−1584	1604	−62°	435	−12°
Fe^{3+}	1300	9.3	1526	1408	2°	50	11°

TABLE VI

APPLICATIONS OF THE SPM TO $KGaF_4:Cr^{3+}$ USING TWO KINDS OF BONDS AND ADJUSTED VALUES OF θ_i AND Φ_i

Cr^{3+}
$\bar{b}_2$ eq = −8960 10^{-4} cm^{-1}, t_2 eq = 1.25
$\bar{b}_2$ ax = −9600 10^{-4} cm^{-1}, t_2 ax = 1.45
θ_1 = 90.75° (+0.3), Φ_1 = 262.5° (0.3)
θ_2 = 88.75° (−0.2), Φ_2 = 82° (0)
θ_3 = 78.15° (−0.3), Φ_3 = 171° (+1.3)
θ_4 = 102° (+0.2), Φ_4 = −7.75° (−0.2)
θ_5 = 170° (−0.1), Φ_5 = 176.8° (1.5)
θ_6 = 10.25 (−0.3), Φ_6 = 10.4° (+1)
b_2^0 = −1545 10^{-4} cm^{-1}
b_2^1 = 3028 10^{-4} cm^{-1}, a_2^1 = −61°
b_2^2 = 460 10^{-4} cm^{-1}, a_2^2 = −17°

Note. The values between parentheses are the deviations from crystallographic data.

Conclusions

In conclusion, in our SPM study of $KGaF_4$ we note a very good agreement between experimental data and calculated values. This probably is the consequence of a small lattice relaxation around the probes, resulting from the closeness of ionic radii of Ga^{3+} and Fe^{3+} or Cr^{3+}. This assumption must be confirmed by studies in other fluogallates.

Other general conclusions, in accordance with previous results (*2–5*) about Fe^{3+} and Cr^{3+}, can be drawn:

For Fe^{3+} ion the spin Hamiltonian axes are very close to the Ga–F bond directions. The main parameter which acts is the length of the ligand bonds and we shall quote a fast decrease of $\bar{b}_2(R)$ when R increases.

For Cr^{3+} ion, the t_2 value must be very small because in this case spin Hamiltonian axes are not bound to the ligand bond directions and angular distortions with a regular octahedron are determinant.

Last, we have detected by ESR a structural phase transition which occurs near 465 K. Actual measurements are in progress.

TABLE VII

APPLICATIONS OF THE SPM TO $KGaF_4:Fe^{3+}$ USING TWO KINDS OF BONDS AND ADJUSTED VALUES OF θ_i AND Φ_i

Fe^{3+}
$\bar{b}_2$ eq = 1080 10^{-4} cm^{-1}, t_2 eq = 10
$\bar{b}_a$ ax = 1810 10^{-4} cm^{-1}, t_2 ax = 12
θ_1 = 91.5° (+1), Φ_1 = 261.1° (−0.8)
θ_2 = 88.6° (−0.3), Φ_2 = 81° (−1)
θ_3 = 78.25° (−0.2), Φ_3 = 171.5° (−0.8)
θ_4 = 101.4° (−0.4), Φ_4 = −8.5° (−1.2)
θ_5 = 168.5° (−1.3), Φ_5 = 176.1° (+0.9)
θ_6 = 11.8° (+1.2), Φ_6 = 11.4° (+0)
b_2^0 = 1522 10^{-4} cm^{-1}
b_2^1 = 1964 10^{-4} cm^{-1}, a_2^1 = 2.4°
b_2^2 = 93 10^{-4} cm^{-1}, a_2^2 = 10.1°

Note. The values between parentheses are the deviations from crystallographic data.

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