

# Elastic Constants of Ammonium Fluoroberyllate by Thermal Diffuse Scattering of X-rays

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## Abstract

All the nine elastic constants of orthorhombic ammonium fluoroberyllate  $[(\text{NH}_4)_2\text{BeF}_4]$  have been determined at room temperature (305 K) from the measurement of the intensities of thermal diffuse scattering of X-rays using a single-crystal diffractometer. Monochromatic Mo  $K\alpha$  radiation obtained by reflection from a curved quartz crystal was used. The intensity of diffusely scattered X-rays has been corrected for divergence, polarization, skew correction, absorption, second-order thermal diffuse scattering and general scattering. Isodiffusion contours have been drawn around the 400 node. The values of elastic constants in units of  $10^{10} \text{ Nm}^{-2}$  are  $C_{11} = 3.82$  (30),  $C_{22} = 3.56$  (28),  $C_{33} = 2.45$  (19),  $C_{44} = 0.96$  (05),  $C_{55} = 1.01$  (05),  $C_{66} = 0.79$  (04),  $C_{12} = 1.78$  (18),  $C_{13} = 1.52$  (15),  $C_{23} = 1.41$  (14). An estimate of the Debye temperature has been made by calculating the mean sound velocity in the crystal from these elastic-constant values.

## Introduction

$(\text{NH}_4)_2\text{BeF}_4$  has been a subject of considerable interest since the discovery of its ferroelectric transition at 175 K (Pepinsky & Jona, 1957) and, more recently, of its non-ferroelectric transition at 182 K (Makita & Yamauchi, 1974). Onodera & Shiozaki (1976) have observed remarkable diffuse scattering in  $\mathbf{a}^*$  and  $\mathbf{c}^*$  directions around reciprocal-lattice points at room temperature in  $(\text{NH}_4)_2\text{BeF}_4$ . A systematic quantitative study of thermal diffuse scattering from  $(\text{NH}_4)_2\text{BeF}_4$  with a view to determining all the elastic constants has been undertaken. The crystals of  $(\text{NH}_4)_2\text{BeF}_4$  are grown by slow evaporation of an aqueous solution. The crystals are soft; and single-domain and twin-free crystals are small in size, as reported in earlier studies (Mukherjee, 1944; Garg & Srivastava, 1979). The method of determining elastic constants of single crystals from a quantitative study of the thermal diffuse scattering (TDS) of X-rays is best suited for such crystals compared to other methods where large single

crystals are needed which are also required to be cut along different directions and polished. This process is likely to introduce strains in the crystals and lead to errors. From three small crystals mounted in different orientations, all the nine elastic constants of  $(\text{NH}_4)_2\text{BeF}_4$  at room temperature in the orthorhombic phase have been determined. This method has previously been applied successfully by several workers: Ramachandran & Wooster (1951*a,b*) for cubic crystals; Prince & Wooster (1953), Prasad & Wooster (1955, 1956), Wooster (1962), Srivastava & Chakraborty (1962) and Phatak, Srivastava & Subbarao (1972) for non-cubic crystals. The crystal structure of this compound has been reported in our earlier paper (Garg & Srivastava, 1979) (Table 1).

## Theory

The ratio ( $\sigma'$ ) of the intensity of diffuse X-rays  $I'_d$  to that of the incident beam  $I_0$ , corresponding to a particular thermal wave vector  $\mathbf{q}$  (where  $|\mathbf{q}| \rightarrow 0$ ), is given by the relation (Laval, 1943; Ramachandran & Wooster, 1951*a,b*)

$$\sigma' = \frac{I'_d}{I_0} = \frac{\varepsilon^2 kT}{V^2} F_T^2 \frac{|\mathbf{X}|^2}{|\mathbf{q}|^2} K[uvw]_{hkl} \delta V,$$

where  $\varepsilon^2$  is the intensity scattered by a free electron and is given by Thomson's formula,  $k$  is the Boltzmann constant,  $F_T$  is the structure factor of the reflection  $hkl$

Table 1. Crystal data on ammonium fluoroberyllate (room temperature)

Chemical formula	$(\text{NH}_4)_2\text{BeF}_4$
Crystal system	Orthorhombic
Axial parameters	$a = 7.6367$ (3) Å $b = 5.9072$ (2) $c = 10.4316$ (3)
Space group	$Pnma$
Number of molecules/cell	4
Volume of the unit cell	470.56 Å <sup>3</sup>
$D_M$	1.686 Mg m <sup>-3</sup>
$D_C$	1.707
Linear absorption coefficient ( $\mu_c$ ) for Mo $K\alpha$	0.24 mm <sup>-1</sup>

at temperature  $T$ ,  $\mathbf{X}$  is the reciprocal-lattice vector corresponding to  $hkl$ ,  $\delta V$  is the volume of the crystal immersed in the X-ray beam and  $V$  is the volume of the unit cell.  $K[uvw]_{hkl}$  is given by

$$K[uvw]_{hkl} = L^2 A_{11}^{-1} + M^2 A_{22}^{-1} + N^2 A_{33}^{-1} + 2MN A_{23}^{-1} \\ + 2NLA_{13}^{-1} + 2ML A_{12}^{-1},$$

where  $L, M, N$  and  $u, v, w$  are the direction cosines of  $\mathbf{X}$  and  $\mathbf{q}$  respectively with respect to orthogonal elastic axes.  $A_{ij}^{-1}$  are the elements of the inverse of the matrix  $A_{ij}$ , which for orthorhombic crystals is given by

$$\begin{bmatrix} A_{11} \\ A_{22} \\ A_{33} \\ A_{23} \\ A_{13} \\ A_{12} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{66} & C_{55} & 0 & 0 & 0 \\ C_{66} & C_{22} & C_{44} & 0 & 0 & 0 \\ C_{55} & C_{44} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{23} + C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{13} + C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{12} + C_{66} \end{bmatrix} \begin{bmatrix} u^2 \\ v^2 \\ w^2 \\ wv \\ wu \\ uv \end{bmatrix}$$

If reflection through a crystal plate from a set of planes nearly normal to its surface is measured through a counter collimator slit subtending a solid angle  $\Omega$  at the crystal, the above equation takes the form (James, 1967)

$$\sigma' = \frac{I'_d}{I_0} = \frac{\epsilon^2 k T \Omega F_T^2 |\mathbf{X}|^2}{V^2 |\mathbf{q}|^2} K[uvw]_{hkl} \\ \times \exp[-\mu_c t \sec \theta] S_0 t \sec \theta,$$

where  $t$  is the thickness of the crystal plate,  $\theta$  is the glancing angle of reflection,  $S_0$  is the area of cross section of the beam; or

$$\sigma = \frac{I_d}{I_0} = \frac{\epsilon^2 k T \Omega F_T^2 |\mathbf{X}|^2}{V^2 |\mathbf{q}|^2} K[uvw]_{hkl}, \quad (1)$$

where  $\sigma$  is now the ratio of the intensity of diffuse reflection (after applying absorption correction) per unit volume of the crystal to the intensity of the incident beam.  $|\mathbf{q}|$  is calculated from the known orientation of the crystal with respect to the incident beam. From the measurement of  $I_d/I_0$ ,  $K[uvw]_{hkl}$  can be evaluated using the above equation. If simple directions  $[uvw]$  of the propagation of the thermal wave and reciprocal-lattice points with simple indices are chosen the corresponding  $K$  may depend on one, two or three elastic constants only. A detailed table of  $K[uvw]_{hkl}$  expressed in terms of elastic constants and the direction cosines of the normals to the reflecting planes for orthorhombic system is given by Wooster (1962). An appropriate number of determinations of such  $K$ 's will thus lead to all the elastic constants.

## Experimental

Single crystals of  $(\text{NH}_4)_2\text{BeF}_4$  were grown by slow evaporation of a saturated aqueous solution at room temperature. These crystals were examined by Laue photographs and polarizing microscope for any strains or multidomains. Defect-free and single-domain plate-type crystals were chosen for the study. The volume of the crystal irradiated by the X-ray beam for each reciprocal-lattice point is given in Table 2. A GEXRD-6 diffractometer equipped with a proportional counter and a single-crystal orienter was used during the course of the experiment. Mo  $K\alpha$  radiation employed for the study was obtained by reflection from a curved-quartz-crystal monochromator. The horizontal and vertical divergence of the beam was 3.58 and 32' respectively. The X-ray tube was operated at 35 kV and 25 mA to avoid higher harmonics ( $\lambda/2$ ,  $\lambda/3$ , etc.). Although we were using small crystals the diffractometer method was preferred over the photographic method as it permits a continuous survey of a whole hemisphere of the reciprocal lattice with smooth and fine controllable motions in much less time, and the intensity measurement is much more accurate. The reciprocal-lattice points used for the evaluation of all the elastic constants were of the type  $h00$ ,  $0k0$ ,  $00l$ ,  $h0l$  and  $0kl$  in different reciprocal planes. These planes along with their structure factors are also listed in Table 2.

Observations for diffuse reflections were made on either side of the Bragg setting for different mis-settings. Time for 10 000 counts was recorded for each mis-setting. Intensity of the direct beam was measured by the method of Prince & Wooster (1953) in which the Compton scattering from diamond is used as an intermediate standard. Compton scattering was measured around the reciprocal-lattice point 220. The accuracy of the measurement of direct-beam intensity was ~3%. For a particular thermal wave vector  $\mathbf{q}$  the corresponding angle for TDS was calculated trigonometrically by considering the geometrical position of the circle of reflection (intersection of sphere of

Table 2. Structure factor data for planes studied in each crystal setting

Plane studied	Axis of rotation	Structure factor	Volume of the crystal in $\text{mm}^3 \times 10$
040	100	55.43	7.406
004	100	72.94	6.875
013*	100	42.13	6.790
004	010	72.94	6.837
200	010	36.31	15.846
301*	010	70.11	15.670
020	001	53.68	7.175
040	001	55.43	7.338

\* In these two cases, the volume was determined graphically.

reflection with the plane of diffraction) in the reciprocal-lattice net for a particular setting of the crystal. The intensity of the observed diffuse reflection  $I_d$  for each  $\mathbf{q}$  was corrected for skew, polarization, divergence, mosaicity and background correction following Ramachandran & Wooster (1951*a,b*) and Amoros & Amoros (1968). The absorption correction was determined graphically by the method of Albrecht (1930) using a theoretically calculated value of  $\mu_c$ . The correction due to second-order thermal diffuse scattering was made for all elastic constants by the method of successive approximation (Ramachandran & Wooster, 1951*a,b*; Lucas, 1968, 1969). Fig. 1 shows the curves relating the intensity of the TDS (after applying corrections) and the square of the wavelength of the thermal wave ( $\lambda^2 = 1/q^2$ ) in sections perpendicular to [100], [010] and [001]. These curves are straight lines passing through the origin. The slopes of these lines give the average value of  $K[uvw]_{hkl}$ .

## Results and discussion

The intensity of diffuse reflections has been measured for thermal waves of short wave vectors ( $\mathbf{q} \rightarrow 0$ ) only. For such wave vectors the frequency of three acoustical modes (one longitudinal and two transverse) approaches zero while that of the optical branch remains high. Owing to equipartition of energy among the various modes of lattice vibration, the amplitude scattered by the optical modes will in general be inappreciable compared to the scattering due to acoustical modes. In some perovskite-type ferroelectrics, there is a low-frequency transverse optical mode, the so-called soft mode, which can contribute significantly to TDS of X-rays. Such a mode is, however, found to be non-existent in  $(\text{NH}_4)_2\text{BeF}_4$ , as has been shown by Popkov, Shabanov, Ermenko & Aleksandrov (1976) and Wada, Sawada, Ishibashi & Takagi (1977) from laser Raman spectra of

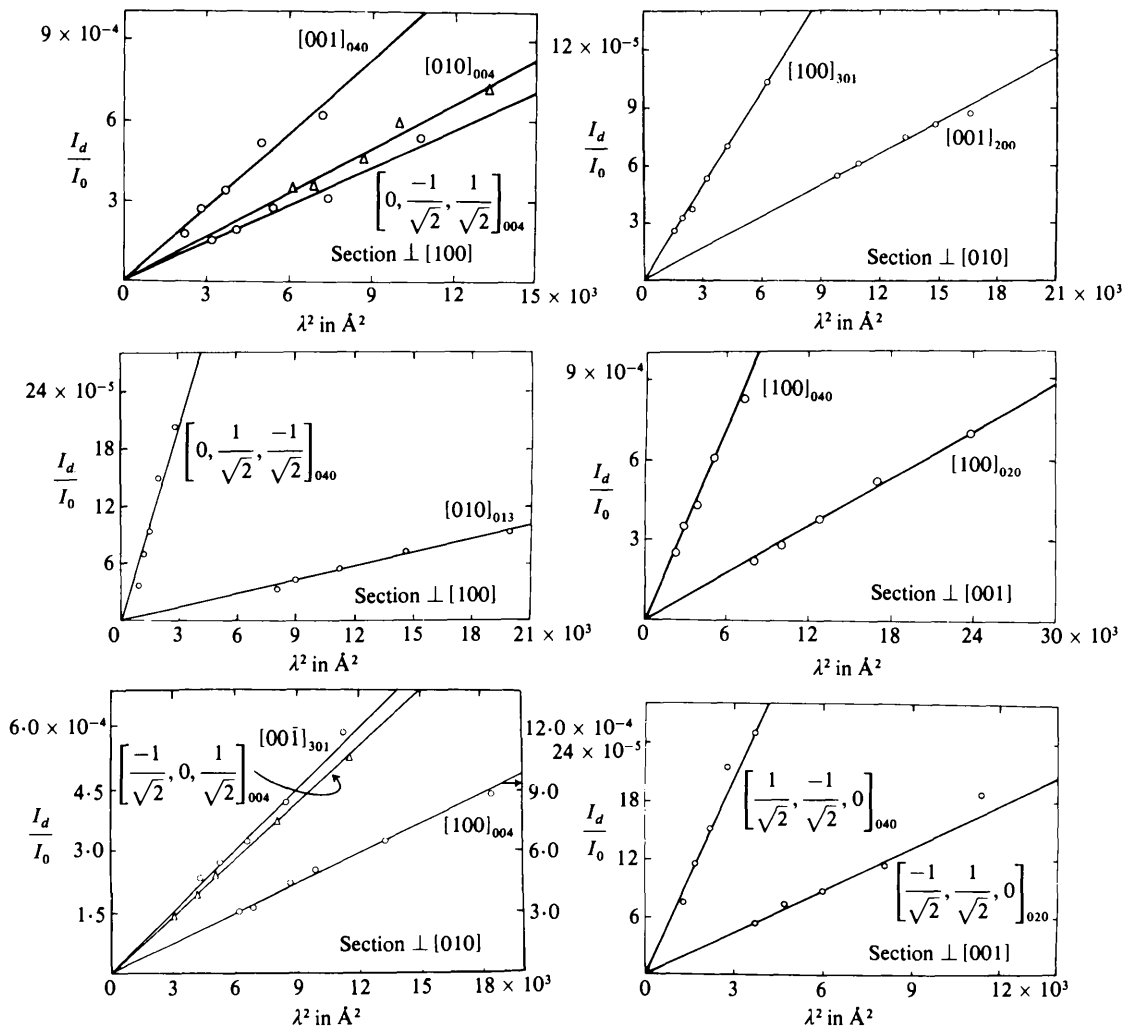


Fig. 1. Variation of diffuse scattering intensity with the square of the wavelength of thermal waves for various directions of the propagation vector and various reciprocal-lattice points.

(NH<sub>4</sub>)<sub>2</sub>BeF<sub>4</sub> at various temperatures from room temperature down to liquid-nitrogen temperature. Hence the contribution of optical modes of vibration to the observed TDS has been neglected.

Each elastic constant is evaluated from at least two different directions of the thermal wave vector. The relation between  $K[uvw]_{hkl}$  and the elastic constants for all reciprocal-lattice points used is given in Table 3. The values of all the elastic constants and  $K[uvw]_{hkl}$  used to evaluate them are listed in Table 4.  $C_{44}$ ,  $C_{55}$ ,  $C_{66}$  were evaluated by measuring intensities of TDS in a direction perpendicular to the reciprocal-lattice vector concerned. They are independent of any other elastic constant. Since the evaluation of all other elastic constants requires the value of  $C_{44}$  or  $C_{55}$  or  $C_{66}$ , each of these has been determined from two reciprocal-lattice points.  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$  could in principle be

Table 3. Relation between  $K[uvw]_{hkl}$  and the elastic constants for the reciprocal-lattice points used

$K[00\bar{1}]_{040}$	$\frac{1}{C_{44}}$
$K[0\bar{1}0]_{004}$	$\frac{1}{C_{44}}$
$K[\bar{1}00]_{004}$	$\frac{1}{C_{55}}$
$K[00\bar{1}]_{200}$	$\frac{1}{C_{55}}$
$K[\bar{1}00]_{020}$	$\frac{1}{C_{66}}$
$K[\bar{1}00]_{040}$	$\frac{1}{C_{66}}$
$K[\bar{1}00]_{301}$	$\frac{L^2}{C_{11}} + \frac{N^2}{C_{55}}$
$K[0\bar{1}0]_{013}$	$\frac{M^2}{C_{22}} + \frac{N^2}{C_{44}}$
$K[00\bar{1}]_{301}$	$\frac{L^2}{C_{55}} + \frac{N^2}{C_{44}}$
$K[\pm\frac{1}{\sqrt{2}}, \pm\frac{1}{\sqrt{2}}, 0]_{020}$	$\frac{2(C_{11} + C_{66})}{C_{11}(C_{22} + C_{66}) + C_{22}C_{66} - 2C_{12}C_{66} - C_{12}^2}$
$K[\pm\frac{1}{\sqrt{2}}, 0, \pm\frac{1}{\sqrt{2}}]_{004}$	$\frac{2(C_{11} + C_{55})}{C_{11}(C_{33} + C_{55}) + C_{33}C_{55} - 2C_{13}C_{55} - C_{13}^2}$
$K[0, \pm\frac{1}{\sqrt{2}}, \pm\frac{1}{\sqrt{2}}]_{040}$	$\frac{2(C_{22} + C_{44})}{C_{22}(C_{33} + C_{44}) + C_{33}C_{44} - C_{23}C_{44} - C_{23}^2}$
$K[0, \pm\frac{1}{\sqrt{2}}, \pm\frac{1}{\sqrt{2}}]_{004}$	$\frac{2(C_{33} + C_{44})}{C_{22}(C_{33} + C_{44}) + C_{33}C_{44} - C_{23}C_{44} - C_{23}^2}$

Table 4. Elastic constant values and the corresponding  $K[uvw]_{hkl}$  from which they have been evaluated

Elastic constant	$K[uvw]_{hkl}$	Elastic constant $\times 10^{-10}$ N m <sup>-2</sup>	Mean $C_{ij}$ $\times 10^{-10}$ N m <sup>-2</sup>
$C_{11}$	$K[\bar{1}00]_{301}$	3.822	3.82 (30)
$C_{22}$	$K[0\bar{1}0]_{013}$	3.555	3.56 (28)
$C_{33}$	$K[00\bar{1}]_{301}$	2.449	2.45 (19)
$C_{44}$	$K[00\bar{1}]_{040}$	0.959	0.96 (05)
	$K[0\bar{1}0]_{004}$	0.963	
$C_{55}$	$K[\bar{1}00]_{004}$	1.016	1.01 (05)
	$K[00\bar{1}]_{200}$	1.008	
$C_{66}$	$K[\bar{1}00]_{020}$	0.771	0.79 (04)
	$K[\bar{1}00]_{040}$	0.814	
$C_{12}$	$K[\pm\frac{1}{\sqrt{2}}, \pm\frac{1}{\sqrt{2}}, 0]_{020}$	1.759	1.78 (18)
	$K[\pm\frac{1}{\sqrt{2}}, \pm\frac{1}{\sqrt{2}}, 0]_{040}$	1.801	
$C_{13}$	$K[\pm\frac{1}{\sqrt{2}}, 0, \pm\frac{1}{\sqrt{2}}]_{004}$	1.520	1.52 (15)
$C_{23}$	$K[0, \pm\frac{1}{\sqrt{2}}, \pm\frac{1}{\sqrt{2}}]_{004}$	1.406	1.41 (14)
	$K[0, \pm\frac{1}{\sqrt{2}}, \pm\frac{1}{\sqrt{2}}]_{040}$	1.416	

determined independently of other constants by measuring the intensity of TDS in the same direction as the reciprocal-lattice vector, but for such wave vectors the geometry of reflection is such that even for the slightest mis-setting from the Bragg angle the value of  $q$  is very large. Thus a small error in the measurement of the angle of mis-setting would introduce large error in  $q$ . Moreover, large  $q$  makes the corresponding value of  $I_d/I_0$  very low and consequently less accurate. It was found to be more so for our crystals as the values of  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$  are quite large compared to other constants. So other reciprocal-lattice points having two non-zero indices had to be used for the evaluation of  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$  making these constants dependent on another elastic constant. Constants  $C_{12}$ ,  $C_{13}$ ,  $C_{23}$  depend on the value of two other elastic constants and so have lower accuracy. The estimated accuracy of  $C_{44}$ ,  $C_{55}$ ,  $C_{66}$ ;  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ ;  $C_{12}$ ,  $C_{13}$ ,  $C_{23}$  is 5; 8; 10% respectively.

Equiscattering contours have been calculated around the reciprocal-lattice point 400 by the method of Jahn (1942) and drawn in Fig. 2. These contours show the variation of elastic vibration amplitudes in different directions of propagation of the thermal wave responsible for the diffuse reflections. These contours have almost circular shape (with a little elongation along  $\mathbf{b}^*$ ) in the  $\mathbf{b}^*\mathbf{c}^*$  plane while they are peanut shaped in the  $\mathbf{a}^*\mathbf{c}^*$  and  $\mathbf{a}^*\mathbf{b}^*$  planes. The elongation of the contour along  $\mathbf{b}^*$  in the  $\mathbf{a}^*\mathbf{b}^*$  plane and  $\mathbf{c}^*$  in the  $\mathbf{a}^*\mathbf{c}^*$  plane shows that the amplitude of vibration of the transverse wave is higher than that of the longitudinal wave. This is found to be true for 040 as well as 004. The contours around 400 depict  $|\mathbf{q}|_{100} < |\mathbf{q}|_{010}$ ,  $|\mathbf{q}|_{100} < |\mathbf{q}|_{001}$  and

$|q|_{001}$  a little  $< |q|_{010}$ , which is in agreement with  $C_{11} > C_{66}$ ,  $C_{11} > C_{55}$  and  $C_{55}$  a little  $> C_{66}$ .

The Debye temperature of  $(\text{NH}_4)_2\text{BeF}_4$  has been calculated using the well known relation

$$\theta_D = \frac{h}{k} \left( \frac{3QND}{4\pi M} \right)^{1/3} \bar{v}_m,$$

where  $Q$  is the number of atoms in the molecule,  $N$  is Avogadro's number,  $D, M$  are the density and molecular weight respectively and  $\bar{v}_m$  is the mean sound velocity in the crystal.

$\bar{v}_m$  has been calculated from elastic constant values using the VRHG approximation (Anderson, 1963). The values of different elastic moduli,  $\bar{v}_m$  and  $\theta_D$ , for  $(\text{NH}_4)_2\text{BeF}_4$  as calculated from Anderson's method are given below:

$$\begin{aligned} \text{bulk modulus} &= 2.077 \times 10^{10} \text{ N m}^{-2}; \\ \text{shear modulus} &= 0.923 \times 10^{10} \text{ N m}^{-2}; \\ \text{Young's modulus} &= 2.410 \times 10^{10} \text{ N m}^{-2}; \\ \bar{v}_m &= 2.599 \times 10^3 \text{ m s}^{-1}; \\ \theta_D &= 389.5 \text{ K}. \end{aligned}$$

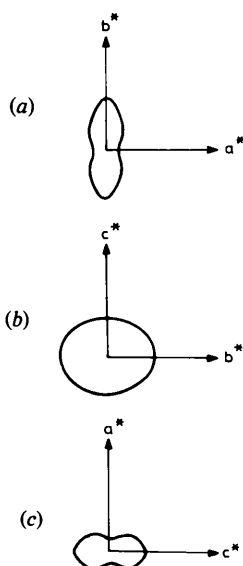


Fig. 2. Equiscattering contours around 400 in (a)  $a^*b^*$ , (b)  $b^*c^*$  and (c)  $c^*a^*$  reciprocal planes.

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