

SHORT COMMUNICATIONS

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Characteristic Debye temperature of ammonium fluoroberyllate, $(\text{NH}_4)_2\text{BeF}_4$. By ANITA GARG and R. C. SRIVASTAVA. *Department of Physics, Indian Institute of Technology, Kanpur 208016, India*

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Abstract

From the elastic stiffness constants C_{ij} of ammonium fluoroberyllate at room temperature, wave velocity surfaces have been calculated and are shown in three different sections (XY, YZ, ZX). The mean sound velocity in the crystal has thus been determined and used to calculate the Debye temperature of $(\text{NH}_4)_2\text{BeF}_4$. The Debye temperature so determined is 381 K. Some of the bulk elastic properties of polycrystalline $(\text{NH}_4)_2\text{BeF}_4$ have also been calculated using the above C_{ij} values.

This is an extension of our earlier work on the crystal structure (Garg & Srivastava, 1979) and elastic constants (Garg & Srivastava, 1980) of ammonium fluoroberyllate [$(\text{NH}_4)_2\text{BeF}_4$] at room temperature using X-ray diffraction techniques. We have now calculated the Debye temperature and some bulk elastic properties of polycrystalline $(\text{NH}_4)_2\text{BeF}_4$ using the above mentioned C_{ij} values. A qualitative correlation between the crystal structure and elastic constants of $(\text{NH}_4)_2\text{BeF}_4$ has also been indicated.

For the Debye temperature, one needs to calculate the mean sound velocity \bar{v}_m in the crystal. \bar{v}_m is defined (Huntington, 1958) as follows:

$$\frac{3}{\bar{v}_m^3} = \frac{I}{4\pi},$$

where

$$I = \int_0^{4\pi} \left\{ \sum_{i=1}^3 [v_i(\theta, \varphi)]^{-3} \right\} d\Omega.$$

In this integral $d\Omega = \sin \theta d\theta d\varphi$; and $v_i(\theta, \varphi)$ are the velocities of the three elastic waves for a given direction (θ, φ) of propagation and the integral is over all directions of propagation. The single-crystal elastic stiffness constants C_{ij} , $v_i(\theta, \varphi)$ and the density ρ of the crystal are related by the well-known Christoffel equations of elasticity theory (Nye, 1957). The values of C_{ij} for $(\text{NH}_4)_2\text{BeF}_4$ and the elastic compliance constants S_{ij} obtained from these C_{ij} 's are listed in Table 1. With these values of C_{ij} 's Christoffel's equation has been solved for v^2 for different values of θ and φ . The Newton–Raphson interactive method has been used to estimate one of the roots. The other two roots are obtained

from the reduced quadratic equation. The nature of the wave velocity surfaces has been shown in different sections (XY, YZ, ZX) for $(\text{NH}_4)_2\text{BeF}_4$ in Figs. 1(a), (b), (c), respectively.

An analytical solution of the integral I is not possible and one has to look for numerical methods to solve it. The approximate numerical method used here is to replace the above integral by a summation of the following type (Robie & Edwards, 1966).

$$\frac{3}{\bar{v}_m^3} = \frac{S}{4\pi} \sum_{\theta=0}^{\theta_s-\Delta\theta} \sum_{\varphi=0}^{\varphi_s-\Delta\varphi} \left(\frac{1}{v_1^3} + \frac{1}{v_2^3} + \frac{1}{v_3^3} \right) \Delta\Omega,$$

where $\Delta\Omega = [\cos \theta - \cos(\theta + \Delta\theta)] \Delta\varphi$ and S is a symmetry constant dependent on the limits of summation θ_s and φ_s . For $(\text{NH}_4)_2\text{BeF}_4$ at room temperature, it is only necessary to integrate over an octant and take $S = 8$. The intervals chosen are $\Delta\theta = \Delta\varphi = 2^\circ$ and $\Delta\theta = \Delta\varphi = 5^\circ$. The difference between \bar{v}_m with the two intervals is found to be negligible (0.1%). All the above calculations have been done on a DEC-10 system. The mean sound velocity thus calculated for $(\text{NH}_4)_2\text{BeF}_4$ is 2.54 km^{-1} . The Debye temperature θ_D is defined as follows (Robie & Edwards, 1966):

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

where n is the number of atoms in the molecule, A is Avogadro's number and ρ, M are the density and molecular weight respectively. The above calculated value of \bar{v}_m substituted in this expression gives 381 K as the Debye temperature for $(\text{NH}_4)_2\text{BeF}_4$.

Table 1. Elastic stiffness (C_{ij}) and compliance (S_{ij}) constants for $(\text{NH}_4)_2\text{BeF}_4$

ij	C_{ij} (GN m ⁻²)	S_{ij} (pN m ⁻²)
11	38.2	0.39
22	35.6	0.41
33	24.5	0.60
44	9.6	1.04
55	10.1	0.99
66	7.9	1.27
12	17.8	-0.13
13	15.2	-0.17
23	14.1	-0.15

Some of the bulk properties of the polycrystalline aggregate, which consists of randomly oriented single crystals of $(\text{NH}_4)_2\text{BeF}_4$, can also be estimated from the single-crystal elastic-constant values (Huntington, 1958). Hill

(1952) has shown by energy density considerations that, for such an aggregate, the Voigt model of calculating bulk modulus from C_{ij} values on the basis of uniform local strain and the Reuss model of calculating bulk modulus from S_{ij} values on the basis of uniform local stress represent the extreme upper and lower bounds and hence an arithmetic average of the two is the best representation of the bulk elastic modulus. Using this simple averaging scheme, called VRHG approximation by Anderson (1963), the different elastic moduli (bulk Modulus K , rigidity modulus G and Young's modulus E) have been calculated for $(\text{NH}_4)_2\text{BeF}_4$ and are listed in Table 2. The average longitudinal (\bar{v}_l) and transverse (\bar{v}_t) velocities of elastic waves in the polycrystalline aggregate are then given by

$$\bar{v} = [(K + \frac{4}{3}G)/\rho]^{1/2} = 4.40 \text{ km s}^{-1}$$

$$\bar{v} = [G/\rho]^{1/2} = 2.32 \text{ km s}^{-1}.$$

Hence the average mean velocity in the polycrystalline $(\text{NH}_4)_2\text{BeF}_4$ is

$$\bar{v}_m = \left(\frac{2}{\bar{v}_l^3} + \frac{1}{\bar{v}_t^3} \right)^{-1/3} = 2.60 \text{ km s}^{-1}$$

giving $\theta_D = 390$ K. This value of \bar{v}_m is in good agreement with the one ($=2.54 \text{ km s}^{-1}$) calculated by the more rigorous integration technique mentioned earlier. This supports the correctness of bulk moduli calculated from the VRHG approximation.

According to the classification of hydrogen-bonded crystals in different structure types by Amoros & Amoros (1968), $(\text{NH}_4)_2\text{BeF}_4$ can be considered as a crystal whose molecules are hydrogen bonded in a three-dimensional framework. It consists of three types of tetrahedra $(\text{NH}_4)_1$, $(\text{NH}_4)_{11}$ and BeF_4 . Their bond lengths and bond angles show that these tetrahedra are almost regular with very little anisotropy in the distribution of bond strength. Hence, one should not expect to observe much variation in the value of the constants C_{11} , C_{22} , C_{33} . Similar results should be expected for C_{44} , C_{55} , C_{66} . Since the Debye temperature is not too high one can expect $(\text{NH}_4)_2\text{BeF}_4$ to be a soft crystal. There is a rough correspondence (Wooster, 1953) between C'_{11} (mean of C_{11} , C_{22} , C_{33}) and hardness H as measured on Mohs' scale. This is given by $C'_{11} = H^{7/4}$. The hardest known substance, diamond, has $C'_{11} = 940 \text{ GN m}^{-2}$ and the corresponding H is ~ 10 . On the same scale corresponding to $C'_{11} = 33 \text{ GN m}^{-2}$ for $(\text{NH}_4)_2\text{BeF}_4$, H is ~ 1.5 . From the crystal structure also one would expect $(\text{NH}_4)_2\text{BeF}_4$ to have low hardness because its molecules are held together by hydrogen bonds which are quite weak as compared with strong covalent bonds in diamond.

Table 2. Elastic moduli (GN m^{-2}) of polycrystalline $(\text{NH}_4)_2\text{BeF}_4$

Modulus	Voigt approximation	Reuss approximation	Mean
Bulk (K)	2.14	2.02	2.08
Shear (G)	0.95	0.90	0.93
Young's (E)	2.37	2.45	2.41
Longitudinal (Y)	3.34	3.28	3.31

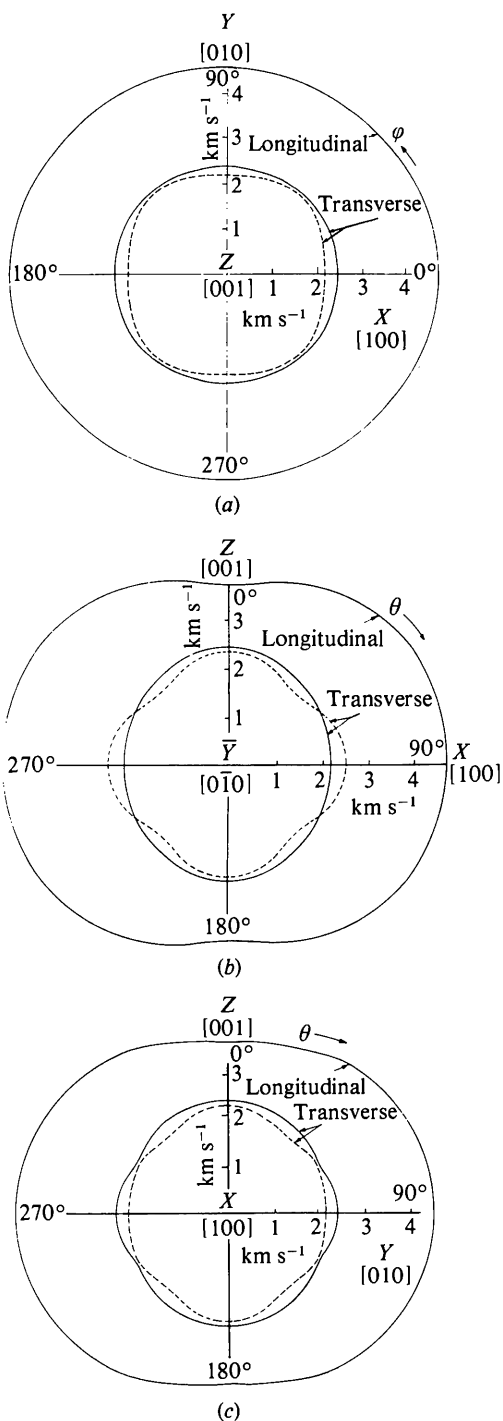


Fig. 1. (a) Cross section of the wave velocity surfaces in (001) of $(\text{NH}_4)_2\text{BeF}_4$. (b) Cross section of the wave velocity surfaces in (100) of $(\text{NH}_4)_2\text{BeF}_4$. (c) Cross section of the wave velocity surfaces in (010) of $(\text{NH}_4)_2\text{BeF}_4$.

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A diffraction pattern caused by thermal diffuse scattering of X-rays in a pyrolytic graphite crystal. By YASUJI KASHIWASE, YOSHIRO KAINUMA and MASAYUKI MINOURA, *Physics Laboratory, Department of General Education, Nagoya University, Chikusa-ku, Nagoya 464, Japan*

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Abstract

A defect line across the 002 diffuse spots scattered from a pyrolytic graphite plate has, for the first time, been clearly observed in X-ray films taken with unfiltered radiation from a copper target. The line was caused by the 002 Bragg reflection of the thermal diffuse scattering.

The present authors have recently succeeded in separating inelastic and elastic scattered intensities and found a dip in the inelastic intensity profile of the 200 Bragg reflection from a LiF crystal (Kashiwase & Minoura, 1981) with energy resolution of about 10^{-8} eV by means of the Mössbauer diffraction with 14.4 keV γ -rays, a nuclear resonant absorber and a position-sensitive proportional detector. The dip was suggested to be caused by the thermal diffuse scattering (TDS) which is secondarily reflected by net planes in the same crystal (Kainuma, 1961). Dips of the same kind were also observed in the 002, 004 and 006 Bragg reflections from KCl (Kashiwase, Kainuma & Minoura, in preparation). The defect line corresponding to the dip was observed in the 002 diffuse spot from a urea nitrate crystal (Kashiwase, Kainuma & Minoura, 1981). The purpose of the present paper is to justify this interpretation by the film observation of the diffraction patterns of X-rays from a pyrolytic graphite crystal. The specimen crystal was chosen for the following reasons. The crystal has a layered structure with a low-lying phonon branch. X-ray film observation of the defect line across the diffuse spot scattered from the crystal was expected to be easy. A dip in the inelastic intensity profile at the 002 Bragg reflection from a pyrolytic graphite plate using 14.4 keV Mössbauer γ -rays has been observed (Zasimov, Lobanov, Rudiger & Kusmin, 1976), although the cause of the dip has been attributed to other effects.

Unfiltered radiation from a copper target in a sealed-off X-ray tube operated at 30 kV and 10 mA was incident with glancing angle θ on a flat surface parallel to the (001) planes of the pyrolytic graphite plate. The plate had a rectangular surface 10×15 mm, thickness 1 mm. The crystal plate was mounted on a goniometer head of a Laue camera. The

incident beam was collimated with a tube of length 60 mm and a hole of diameter 0.5 mm. The distance between the source and the crystal was about 130 mm. The camera length between the crystal and the film was about 100 mm. X-ray films for cosmic-ray observations were used.

Figs. 1(a) and (b) show X-ray diffraction patterns taken at glancing angles of 13.3° and 15.3° , respectively. The schematic illustration of these patterns are shown in Figs. 2(a) and (b). The large spot *A* and the small one *B* were caused by the TDS of $K\alpha$ and $K\beta$ X-rays near the 002 reciprocal-lattice point, respectively. Figs. 1(a) and 2(a) show the case in which the glancing angle θ nearly equals the Bragg angle $\theta_b = 13.3^\circ$ for the 002 reflection of Cu $K\alpha$ radiation. The spot *E* is due to the incident beam penetrating the crystal and a thin lead sheet set before the film. The sharp long defect line *D* is clearly seen across the middle of the diffuse spot *A* and the Laue spot *C*. In Figs. 1(b) and 2(b), the deviation angles between the spot *A* and the line *D* and between the spot *C* and the line *D* are the same. They are

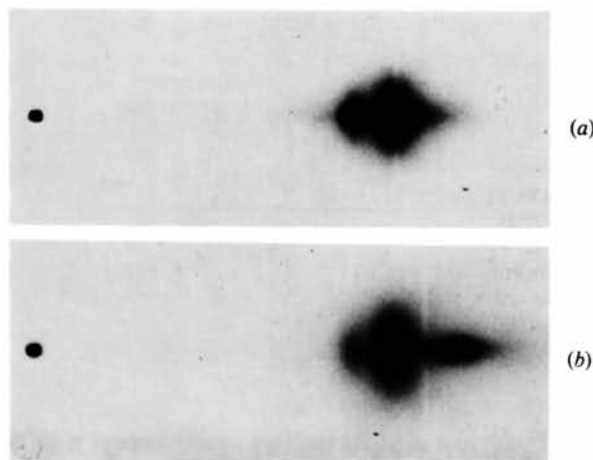


Fig. 1. X-ray diffraction pattern of pyrolytic graphite. The dimensions of the figures are those of the original ones.