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Diffuse X-ray Scattering from Crystals of Hexamminecobalt(III) Nitrate

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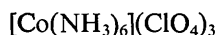
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Crystals of hexamminecobalt(III) nitrate are found not to be cubic like those of the thiocyanatopentamine derivative but to be tetragonal and of space group symmetry $P4_2nm$. The unit-cell parameters are $a = b = 21.66$, $c = 33.32 \pm 0.05$ Å. The most prominent feature of the difference in response to X-rays of these and similar crystals is the heavy diffuse scattering produced by the hexamminecobalt(III) nitrate. By means of a series of cylindrical Laue photographs, taken with monochromatic cobalt ($\text{Co } K\alpha$) radiation, covering a quadrant of reciprocal space at regular intervals of 5° about the tetragonal axis, the diffuse domains in the reciprocal lattice are explored and information obtained on the nature and direction of propagation of the thermal waves in the crystal. An interesting feature of the crystal dynamics of hexamminecobalt(III) nitrate is that the only effects observed as a result of independent motion of large structural units are those of transverse waves. There are no noticeable similar effects ascribable to longitudinal waves. Thus information is obtained on the behaviour, shape and orientation of the structural units $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $(\text{NO}_3)^-$.

Introduction

It has been observed by Fletcher & McDoom (1967) that in the crystal of the inorganic salts of the hexamine and pentamine complexes of cobalt and related metals the symmetry of each crystal depends on (i) the effective symmetry of the complex cation, and (ii) the nature and symmetry of the anion or anionic components. On the basis of a study of the X-ray diffraction spectra, they suggested further that in the cubic crystals of aquopentamminecobalt(III) perchlorate $[\text{Co}(\text{NH}_3)_5 \cdot \text{H}_2\text{O}](\text{ClO}_4)_3$ the complex ion $[\text{Co}(\text{NH}_3)_5 \cdot \text{H}_2\text{O}]^{3+}$ exhibits ellipsoidal rotation.

This is consistent with the report by Hassel & Bödtker Naess (1928) that these crystals as well as those of hexamminecobalt(III) perchlorate



are cubic.

However, in the case of hexamminecobalt(III)

nitrate $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ and its monosubstituted thiocyanato derivative $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{NO}_3)_2$, the former is not cubic while the latter is. The symmetry of the crystals of the hexamine compound has been found, as will be described presently, to be tetragonal and that of space group $P4_2nm$; while that of the corresponding thiocyanatopentamine compound was determined (though not reported) by Price & Fletcher (1965), and confirmed in the course of these investigations to be cubic and that of space group $Fm\bar{3}m$.

Moreover, one of the most distinctive features of the response to X-rays of these crystals and others being studied in this laboratory is the heavy diffuse scattering produced by the crystals of hexamminecobalt(III) nitrate, as opposed to the others.

It has been shown by Laval (1938, 1939a,b) and Lonsdale (1942, 1942-3), and others, that the diffuse scattering produced by simple crystals is essentially of thermal origin resulting from the vibrations of the individual atoms or monatomic ions; and is of two types, appearing on photographs as: (i) spots and (ii) streaks, whose maxima in both cases are always found to be on the unforbidden reciprocal lattice points.

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From molecular crystals, the diffuse scattering comprises – in addition to spots and streaks – yet a third type, diffuse domains, which extend over a relatively large volume of reciprocal space and may be found to cover several reciprocal lattice points, even forbidden ones.

These extended domains of diffuse scattering have been shown by Amoros & Canut (1957, 1958*a,b*, 1960), Amoros, Canut & de Acha (1960) and Banerjee, Canut & Amoros (1961) to be due to independent vibrations and librations of large structural units in the crystals. We observed that there was a striking similarity between the diffuse pattern obtained from hexaminecobalt(III) nitrate crystals and those obtained by Amoros and co-workers from the long chain molecular crystals.

Thus the study reported here of the diffuse scattering from crystals of hexaminecobalt(III) nitrate was undertaken to investigate the behaviour of the ions, particularly that of the complex cation $[\text{Co}(\text{NH}_3)_6]^{3+}$.

Symmetry and lattice parameters

Polarization microscopy indicated that the crystals of hexaminecobalt(III) nitrate are tetragonal. A positive pyroelectric test, confirmed by anomalous X-ray diffraction of Cu $K\alpha$ radiation, revealed that the crystals are noncentrosymmetric.

Rotation and Weissenberg photographs, taken with filtered cobalt (Co $K\alpha$) radiation and the crystals rotating about the [001] and [100] axes, showed the observed spectra to be consistent with the following systematic restrictions:

hkl	none
$hk0$	none
$0kl$	$k+l=2n$
$h0l$	$h+l=2n$
hhl	none

Thus the crystal symmetry is that of space group $P4_2nm$.

The lattice parameters were determined from the $\alpha_1\alpha_2$ separations on Weissenberg photographs and found to be $a=b=21.66$, $c=33.32 \pm 0.05$ Å.

Investigation of the diffuse scattering

The diffuse scattering of monochromatic (filtered) Co $K\alpha$ radiation was recorded on Laue photographs with the film in cylindrical form. Each exposure was taken for 3 hours at 40 kV and 8 mA, with the [001] axis of the crystal coincident with that of the goniometer.

The diffuse domains in reciprocal space were thus explored by means of a series of such photographs covering altogether a range of 90° , at 5° intervals about the tetragonal axis; and the diffuse scattering domains on each reciprocal lattice level $[001]_n$ plotted. This was done by measuring the cylindrical coordinates

ξ and ζ of the diffuse reflexions on each reciprocal lattice level with the aid of a Martin's (1956) chart. The orientation of the crystal with respect to the X-ray beam was then determined by comparing the diffuse domains on each level of the reciprocal lattice with the corresponding reciprocal lattice net, since the thermal diffuse scattering maxima must be coincident with the reciprocal lattice points.

Diffuse scattering domains in the levels $[001]_n$

The diffuse scattering obtained from this crystal is shown in Fig. 1, and consists of:

- streaks perpendicular to the equatorial line and extended across several layer lines of the corresponding rotation photograph, *i.e.* across several reciprocal lattice levels;
- round and definite spots of varying intensities, giving diffuse clouds around non-forbidden reciprocal lattice points.

The $[001]_0$ level

The diffuse domains in the $[001]_0$ level are shown in Fig. 2. The strongest round diffuse spots are associated with the reciprocal lattice points $\{520\}$. There are some moderately strong continuous diffuse domains of rectangular form, with one dimension much longer than the other, at the reciprocal lattice points $\{660\}$ and $\{12,12,0\}$ the more intense ones being at $\{660\}$. Continuous diffuse scattering domains appear along rows of reciprocal lattice points having h constant, and k constant the most intense being those for $h=8$ and $k=8$.

The $[001]_1$ and higher levels

The diffuse reflexions were plotted in the $[001]_1$ (Fig. 3) and higher levels to investigate whether the

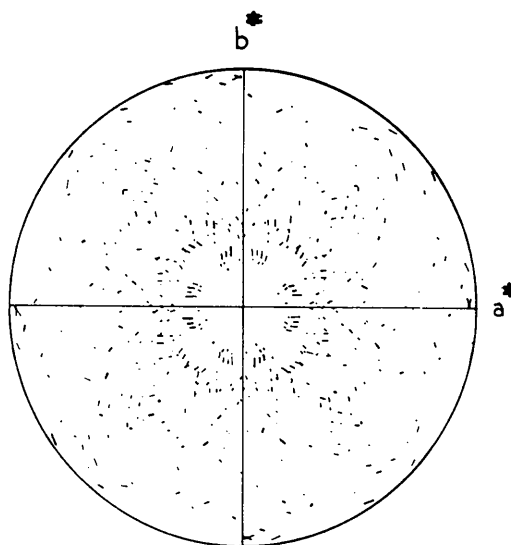


Fig. 2. The diffuse domains in the level $[001]_0$.

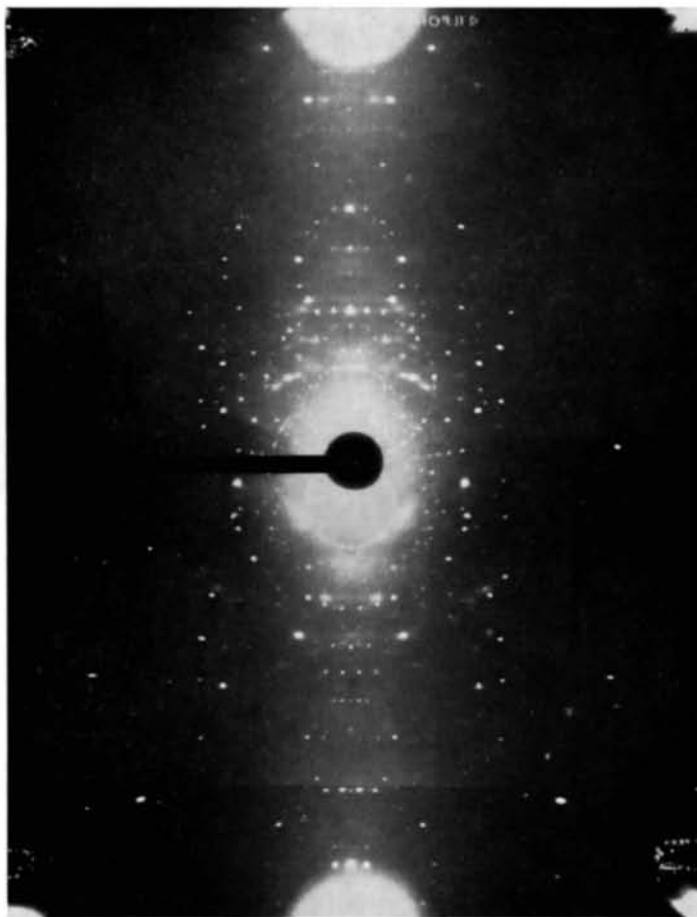


Fig. 1. Laue photograph with Co *K* α of hexamminecobalt(III) nitrate with the [001] axis of the crystal parallel to the goniometer axis and the [001] axis inclined to the X-ray beam at an angle of 90°.

continuous diffuse domains extend across the layers. No inter-layer plotting was done as the inter-layer separation for this crystal was considered too small to warrant this.

Three-dimensional analysis of the diffuse scattering

Analysis of the domains of the extended continuous diffuse scattering, reveals that there are two types of such domains:

- (i) Sheets perpendicular to the equivalent axes a and b
- (ii) Rods perpendicular to the direction $\langle 110 \rangle$.

Propagation of waves

It has been shown and explained by Lonsdale (1948) that the shape and extension of the diffuse scattering domains in the reciprocal lattice depend on the various kinds of thermal waves propagated through the crystal, and that the diffuse scattering domains always extended in reciprocal space along the direction of propagation of the waves – whether longitudinal or transverse.

While the effects of transverse waves due to the independent motion of large structural units were observed in this crystal, it is significant that no such effects were observed that are ascribable to longitudinal waves.

The absence of effects arising from such longitudinal waves is shown in Fig. 4, in which the effects of the different types of waves on the distribution of diffuse scattering in the reciprocal lattice are illustrated as follows:

- (i) The effects only of transverse waves propagated along the directions perpendicular to the b and a axes provided there are elongated structural units aligned parallel to each of these axes and under-

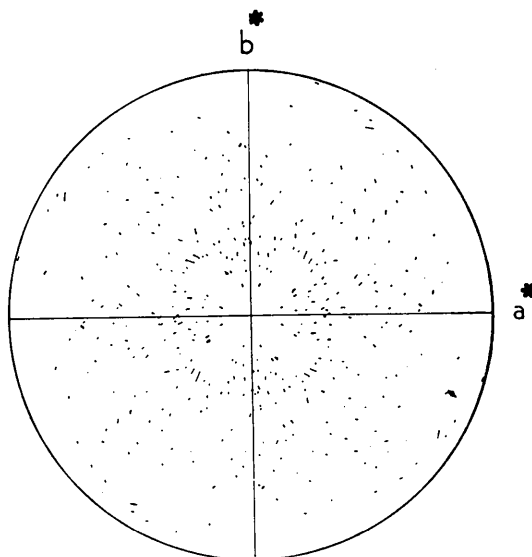


Fig. 3. The diffuse domains in the level $[001]_1$.

going relatively independent vibrations are shown in Fig. 4(a).

- (ii) The effects due to longitudinal waves alone arising from atomic vibrations propagated along the directions $\langle 520 \rangle$ are shown in Fig. 4(b); while those only from transverse waves due to atomic vibrations propagated along the same directions $\langle 520 \rangle$ are shown in Fig. 4(c).
- (iii) Finally, in Fig. 4(d) is shown the diffuse scattering domains in the zero level $[001]_0$ of the reciprocal lattice due to the combined effect of all the waves mentioned above.

The relative lengths of the traces in Fig. 4 are simply a guess to account for the extensions (lengthwise and breadthwise) of the observed diffuse domains. In the case of the elliptic diffuse domains associated with the reciprocal lattice points $\{520\}$ these extensions are along the directions $\langle 520 \rangle$ in the reciprocal lattice; thus the waves (longitudinal and transverse) propagated in the crystal along these directions are responsible for the observed extensions.

Discussion of results

The similarities between the pattern of diffuse scattering obtained from the crystal under study and those obtained by Amoros *et al.* and Banerjee *et al.* from the long chain molecular crystals suggest that we may obtain interesting information regarding the dynamics of our crystal, as well as the shape and orientation of the important structural units, by comparing different aspects of our results with those of Amoros *et al.* and Banerjee *et al.*

Amoros & Canut (1957) noticed that there was a marked resemblance between the diffuse intensity and the Difference Fourier Transform (DFT) of the molecules. The DFT is just the difference between intensities of the radiation scattered by the molecules of a unit cell at rest and in motion. In calculating the DFT it is assumed that the thermal excitation causes the molecules to make independent translational vibrations as rigid units. Even before Amoros *et al.*, Charlesby, Flinch & Wilman (1939) in their studies of the diffuse electron diffraction pattern from anthracene crystals noticed the relation between the Fourier transform of the molecules and the thermal scattering. Cochran (1956) had shown that the diffuse scattering from a crystal with defects has an intensity equal to the difference of the square of the Fourier transforms of the perfect and imperfect crystal, except at the reciprocal lattice points. The correspondence between Cochran's idea and that of Amoros *et al.* becomes evident if we consider the Fourier transform of the perfect crystal to be that at absolute zero and the Fourier transform of the imperfect crystal to be that at the temperature of the experiment; the imperfection of the crystal being considered to be due to thermal vibrations of the atoms and molecules only.

The first theory of diffuse scattering of X-rays by molecular crystals along the line of the established theory of lattice dynamics as given by Laval (1941) is due to Hoppe (1956, 1957). Hoppe shows that a molecular crystal can be treated as though the whole molecule were replaced by a single point-like scatterer. From Hoppe's theory it follows (Wooster, 1962) that for regions of reciprocal space far from 'relps' the scattering should be the same as that given by a point-like scatterer multiplied by the Fourier transform of the molecules in the unit cell; and that for regions roughly mid-way between 'relps', the intensity of the scattering can be considered as a result of independent vibrations of the molecules. Thus the

DFT approach of interpreting the continuous extended diffuse scattering domains is not totally alien to the usual lattice dynamical approach. More recent theories on lattice dynamics of molecular crystals have been given by Sandor (1962), Cochran & Pawley (1964), and Hahn & Biem (1963). Of these, Cochran & Pawley's theory seems to be more detailed and can be employed more readily for numerical calculations. They have, in fact, presented numerical calculations for hexamethylenetetramine (hexamine) on the basis of their theory. They have calculated the thermal diffuse scattering for the zero layer $[0k1]$ and the first interlayer $[\frac{1}{2}k1]$, and then have compared the results of their calculations with the corresponding experimental

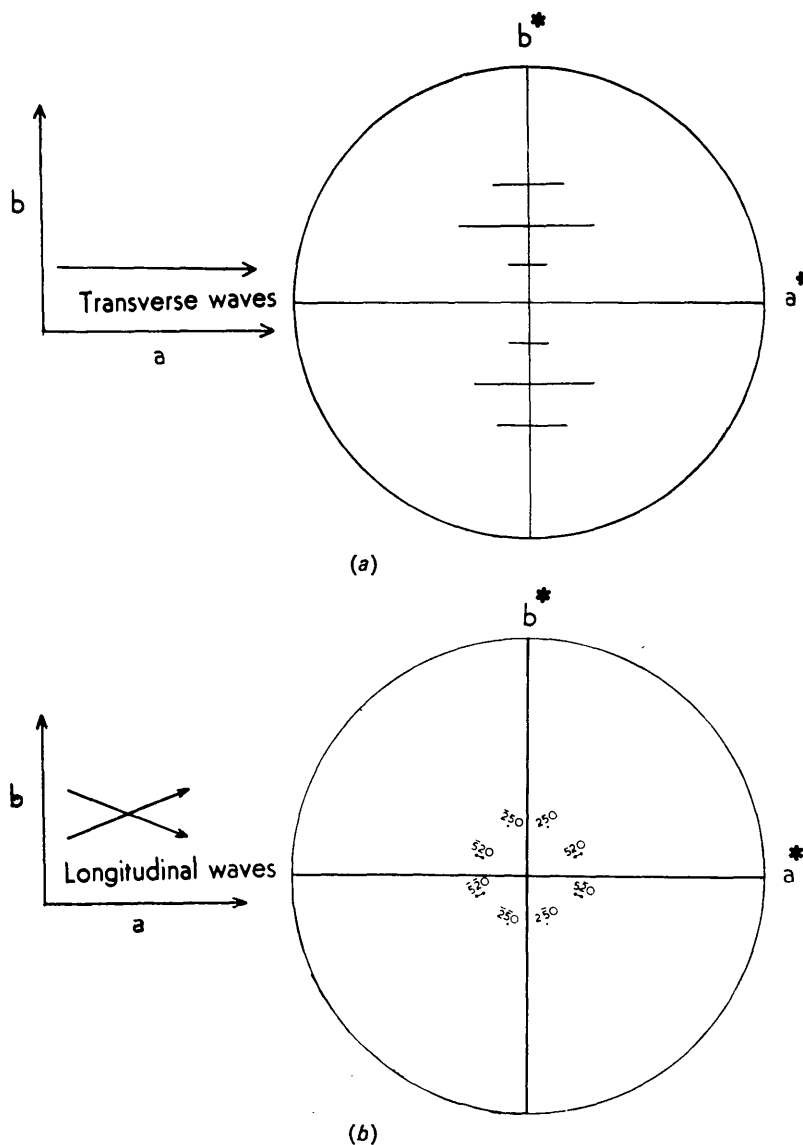


Fig. 4. (a) The diffuse pattern in reciprocal space due to the effect of *transverse* waves whose direction of propagation is perpendicular to the directions of the b and a axes. (b) The diffuse pattern in reciprocal space due to the effect of *longitudinal* waves arising from atomic vibrations and propagated along the directions $\langle 520 \rangle$ and $\langle 250 \rangle$.

results of Amoros, Canut & de Acha (1960) as well as with the corresponding DFT. They found that the calculations based on their theory gave results which agreed well with the experimental results of Amoros *et al.* and were also in qualitative agreement with the DFT representation. Another point of interest in their findings is that the diffuse intensity calculated on the basis of their theory is in semi-quantitative agreement with the intensity calculated on the basis of the theory of Becka & Cruickshank (1963*a,b*) which suffers from a serious defect, inasmuch as it gives dispersion curves which do not satisfy the result that dispersion curves have zero gradient at all Brillouin zone boundaries. These facts show that the general

aspects (forms and extensions) of the extended and continuous diffuse domains obtained from molecular crystals do not depend markedly on the detailed aspects of the lattice dynamics.

It has been observed by Rolland-Gaillard (1965) that thermal diffuse scattering away from the 'relps' does not vary appreciably, even for the simple crystal like NaCl, when very different types of force field are assumed to exist in the crystal, although dispersion curves corresponding to these different types of field vary rather wildly.

Thus we are led to believe that in the rather qualitative studies of our crystal we can look upon the problem from Amoros's point of view inasmuch as the

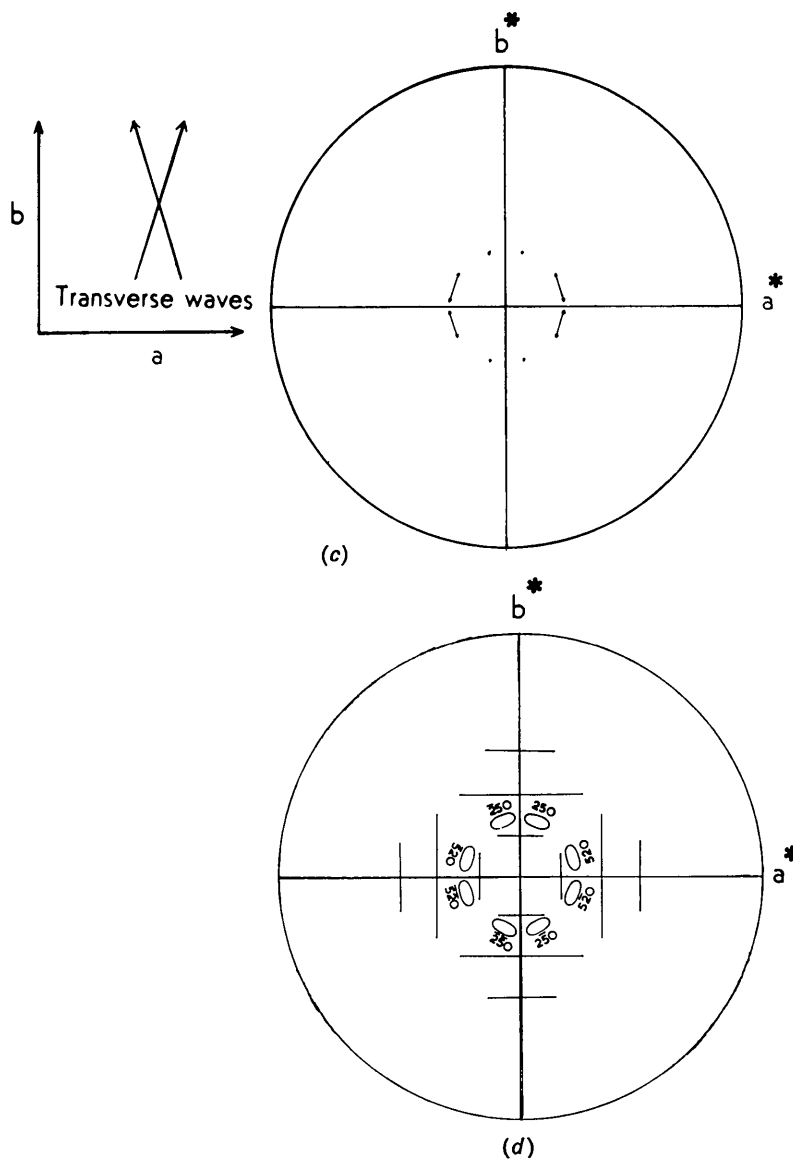


Fig.4. (cont.) (c) The diffuse pattern in reciprocal space due to the effect of *transverse* waves arising from atomic vibrations and propagated along the directions $\langle 520 \rangle$ and $\langle 250 \rangle$. (d) The resultant diffuse scattering domains in the zero level $[001]_0$ of the reciprocal lattice of hexamminecobalt(III) nitrate due to the combination of the effects illustrated in Fig.4(a)-(c).

general features of the results obtained by us are similar to those obtained by Amoros *et al.*

From this it follows that important parts of the crystal dynamics of hexamminecobalt(III) nitrate $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ consist of independent rigid body vibrations of important structural units, *i.e.* the sets of ions. Further, the sheet and rod-like diffuse domains suggest that some of the structural units are elongated while others are planar *i.e.* the $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $(\text{NO}_3)^-$ ions respectively.

From the orientations of these diffuse domains it follows (as is shown in Fig.4) that the elongated $[\text{Co}(\text{NH}_3)_6]^{3+}$ ions have their long axes parallel to the *a* and *b* axes of the crystal, while planar units $(\text{NO}_3)^-$ are normal to the *ab* plane and aligned along the diagonals in this plane. Finally, the strong elliptic diffuse domains associated with the relps $\{520\}$ can be thought of [as shown schematically in Fig.4(b), (c) and (d)] as being due to the thermal waves arising out of the atomic vibrations (being different from the independent molecular vibrations) propagated along $\langle 520 \rangle$ directions of the reciprocal lattice.

We have postulated independent rigid body vibrations of the structural units of the crystal under study in order to interpret the marked similarities between the observed diffuse pattern from this crystal and those from the long chain molecular crystals observed by Amoros *et al.*

Molecular crystals are characterized by weak binding. Probably this is also the reason why the thermal diffuse scattering from molecular crystals can be approximately interpreted by postulating independent vibrations of the molecules.

The fact that hexamminecobalt(III) nitrate gives diffuse scattering patterns similar to those from molecular crystals, suggests that probably interionic binding in this case also is quite weak.

Comments

The investigation of the behaviour of the complex ion in this and similar crystals is being pursued by means of crystal structure analysis, the study – particularly in the case of hexamminecobalt(III) nitrate – of the diffuse X-ray scattering by means of Difference Fourier Transforms as described by Amoros & Canut (1958 *a,b*) and Banerjee *et al.* (1961), as well as

the study of their elastic properties by means of diffuse X-ray scattering.

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