tétraèdre d'oxygènes. Cette préférence pour une position tétraédrique est telle que Zn ne peut entrer dans la constitution des boroferrites où tous les voisinages sont octaédriques.

Nous terminons par un résumé (Tableau 1) des groupes spaciaux et paramètres des boracites étudiés jusqu'ici, Les résultats des chercheurs japonais y sont inclus.

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Tableau 1. *Groupes spaciaux et paramètres des boracites*

Formule	Groupe spatial	a (A.)	b (A.)	c (A.)	v (A.^{3})	d
$B_2O_3,Fe_2O_3,4FeO$	D_{2h}^9–$Pbam$	9·44	12·26	3·065	354·7	4·808
$B_2O_3,Fe_2O_3,4CoO$		9·35	12·28	3·03	348·7	5·018
$B_2O_3,Fe_2O_3,4NiO$		9·248	12·26	3·01	341·3	5·107
$B_2O_3,Fe_2O_3,4CuO$		9·397	12·02	3·13	353·5	5·112
$B_2O_3,Fe_2O_3,3MgO,(Fe,Mg)O$ (ludwigite I)		9·14	12·45	3·05	347	3·86
$B_2O_3,Fe_2O_3,2MgO$ (ludwigite II)	D_{2h}^{16}–$Pnam$	9·258	9·427	3·104	270·9	3·78
$B_2O_3,Fe_2O_3,2FeO$		9·243	9·468	3·158	276·4	4·45
$B_2O_3,Fe_2O_3,2CoO$		9·243	9·39	3·135	272·1	4·60
$B_2O_3,Fe_2O_3,2NiO$		9·141	9·351	3·047	260·4	4·80
$B_2O_3,TiO_2,3MgO$ (warwickite)		9·20	9·45	3·01	262	—
$B_2O_3,Mn_2O_3,3MgO,MnO$ (pinakiolite)	C_{2h}^2–$P2_1/m$	5·36	5·98	12·73	$\beta = 120° 34'$	

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The X-ray scattering from a hindered rotator.

By THOMAS H. WALNUT, JR., and GENE B. CARPENTER, *Metcalf Research Laboratory, Brown University, Providence, Rhode Island, U.S.A.*

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In a recent paper under this title, King & Lipscomb (1950) derived the geometric part of the molecular structure factor for an atom executing hindered rotation in the form

$$M_n^\gamma(a,b)=\int_0^{2\pi} P(\theta)\exp\left[ia\cos\theta\right]d\theta.$$

Their notation is used here and throughout. $P(\theta)\,d\theta$ is the probability that the atom be in the angular range $d\theta$ and the exponential is the contribution from an atom in this range. They stated, but did not prove, that for an infinite hindering potential ($b=\infty$) this becomes

$$M_n^\gamma(a,\infty)=(1/n)\sum_{m=1}^{n}\exp\left[ia\cos\left(\gamma+2\pi m/n\right)\right],$$

where n is the number of minima in the potential and γ is the rotation angle corresponding to a minimum. The purpose of this note is to outline a simple proof.

For convenience, let $\phi=\theta-\gamma$ in the probability function:

$$P(\phi)=\frac{\exp\left[b\cos n\phi\right]}{\int_0^{2\pi}\exp\left[b\cos n\alpha\right]d\alpha}.$$

Consider the case $0<\phi\leqslant\pi/n$. In consequence of the symmetry, the denominator D may be rewritten as

$$D=2n\int_0^{\pi/n}\exp\left[b\cos n\alpha\right]d\alpha.$$

A quantity ϵ can always be found such that $0<\epsilon<\phi$, then these inequalities hold:

$$D\geqslant 2n\int_0^{\epsilon}\exp\left[b\cos n\alpha\right]d\alpha\geqslant 2n\exp\left[b\cos n\epsilon\right]\epsilon.$$

Therefore $$P(\phi)\leqslant\frac{\exp\left[b(\cos n\phi-\cos n\epsilon)\right]}{2n\epsilon}.$$

Now in the range considered, $\cos n\phi-\cos n\epsilon=-|c|$, where c is a finite constant for given ϕ and ϵ. Therefore

$$\lim_{b\to\infty}P(\phi)\leqslant 0.$$

But since by definition $P(\phi)$ is always positive,

$$\lim_{b\to\infty}P(\phi)=0\quad(0<\phi\leqslant\pi/n).$$

By symmetry, this result applies also for any $\phi\neq 2\pi m/n$, $m=1,2,\ldots,n$.

Also, from the definition,

$$\int_0^{2\pi}P(\alpha)\,d\alpha=1.$$

Comparison of the last two equations with the equations defining the Dirac δ-function (Dirac, 1947, p. 58) permits the conclusion

$$\lim_{b\to\infty}P(\phi)=(1/n)\sum_{m=1}^{n}\delta(\phi-2\pi m/n).$$

Replacing ϕ by $\theta-\gamma$

$$\lim_{b\to\infty}P(\theta)=(1/n)\sum_{m=1}^{n}\delta(\theta-\gamma-2\pi m/n).$$

This result can now be inserted into the expression for M:

$$\lim_{b\to\infty} M_n^\gamma(a,b) = \int_0^{2\pi} \exp[ia\cos\alpha] \lim_{b\to\infty} P(\alpha)\,d\alpha,$$

$$M_n^\gamma(a,\infty) = (1/n)\int_0^{2\pi} \exp[ia\cos\alpha] \sum_{m=1}^{n} \delta(\alpha-\gamma-2\pi m/n)\,d\alpha$$

$$= (1/n)\sum_{m=1}^{n} \exp[ia\cos(\gamma+2\pi m/n)],$$

which is the desired result. The δ-function argument may, of course, be replaced by well-known limiting processes.

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Vector maps of hydrated protein crystals.*

By DOROTHY WRINCH, *Department of Physics, Smith College, Northampton, Mass., U.S.A.*

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The difficulty of attempting structure analyses of protein crystals by studying the intensities recorded in X-ray diffraction studies has focussed attention on their vector maps. This note is concerned with the significance, for these vector maps, of the considerable complements of water in protein crystals.

We picture a crystalline protein as an array of molecules in a medium in atomic space S. To a first approximation, the medium may be represented by a constant m and the electron-density function $g(x,y,z)$ will take the value m over the intermolecular regions in the cell. Let us suppose that the same molecules crystallize in the same medium to form a series of hydrates, each with its own unit cell. Then a separate g is required for each hydrate and the question arises as to a method whereby the problem of calculating the functions $g_v(x,y,z)$ defining the vector maps can be treated *as a whole*. A schematic representation of such a situation is seen in Fig. 1 in which a and c are 'crystals' in which the same 'molecule' crystallizes in the same 'medium' ($m=1$); in A and C the corresponding maps in vector space S_v are separately calculated. It is evident that the problem is not solved simply by using the finite vector map of the common molecule, which is shown between A and C. To it we should need to add the vector map of the medium and the interactions of the medium and the molecule; these maps necessarily differ from crystal to crystal. However, progress can be made if we focus attention not on the common molecule but on the common medium. Accordingly we record, in b and d, the crystals reduced to the level of the medium, defined by the reduced density functions $r_m(x,y,z)=g(x,y,z)-m$. Each crystal is now represented simply by the original molecule reduced to the level m, as shown between b and d. For this reduced molecule, the vector map is recorded, once for all. Inserting this map in the appropriate orientation at given sets of lattice points, the vector maps of the reduced crystals are obtained as shown in B and D. To see the relation between the vector map of a reduced crystal and the vector map of the original crystal, we recall the theorem (Wrinch, 1939) that the vector maps of a crystal defined by $g(x,y,z)$ and by $g(x,y,z)-k$ are represented by $g_v(x,y,z)$ and by $g_v(x,y,z)-k_v$, where k_v is such as to make the total weight in the cell in S_v equal to the square of the total weight in the cell in S in each case. If there are n entries in the cell, we may write w and $w-nk$ for the total weight in S and $w_v\ (=w^2)$ and w_v-nk_v for the total weights in S_v. It then follows that

$$w_v-nk_v=(w-nk)^2, \quad k_v=k(2w-nk).$$

In the figure we see an example of this theorem by comparing B with A and D with C.

It is thus possible to formulate the vector maps for crystals in which molecules are arrayed in a constant medium by studying the crystals reduced to the level of the medium, and it is sufficient to record simply the vector maps of the reduced crystals since each is the vector map of the original crystal reduced to a certain level. The examples in Fig. 1 confine attention to the case of one molecule in the unit cell, and the only preliminary to writing down the vector maps is the vector map of the molecule reduced to the m level. This procedure may be extended to cover any number of molecules. When the crystal reduced to the level m comprises reduced molecules $M_1, M_2, \ldots$, it is sufficient to construct in addition the maps assembling vectors between each of these and every other and so obtain the synthetic vector maps of proposed structures of a whole series of crystals. Further, the method can be extended to deal with media at different levels.

To test a proposed structure of a crystal on the intensities we have to compare the synthetic vector map with the 'experimental' vector map, which is the Fourier transform of these intensities. All the experimental vector maps of protein crystals which are recorded in the literature are calculated from relative intensities and thus correspond to distributions in S on an unknown scale. It is possible to make rough estimates of the number of electrons in the unit cell. However, the scale on which the square of this number is to be inserted at the origin is unknown. Thus in all these calculations $I(000)$ is perforce taken to be zero. It results that all such experimental vector maps are reduced vector maps with total weight $w_v=0$ and the distributions in S about which they afford information are reduced crystals, in which an electron density $g(x,y,z)$—on an unknown scale—is replaced by $r(x,y,z)=g(x,y,z)-\bar{g}$ to yield a total weight $w=0$. Hence these experimental vector maps relate to electron-density deviations in atomic space S, deviations from the average $\bar{g}$, not to

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