Short Communications

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Anion dipole contribution to the lattice energy of rutile*.

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Permanently polarized anions in crystals possessing the rutile structure contribute extra terms to the lattice energy of such crystals. The dipole term has been calculated for TiO_2 and estimated for the fluorides. This term is not large enough to account for the difference between the theoretically and experimentally determined lattice energies of rutile-type crystals.

Baur (1961) has calculated the Madelung constant and lattice energy of crystals with the rutile structure by the Ewald method. He suggests that the large discrepancy between some of his calculated lattice energies and the Born–Haber values implies that the crystals are non-heteropolar. This is the case for TiO_2, GeO_2, SnO_2 and FeF_2. On the other hand, he finds better agreement between his calculations and Born–Haber results in the cases of MgF_2, MnF_2 and ZnF_2.

It is interesting to note that in every case cited the energy calculated theoretically is less than that determined experimentally. For the fluorides the difference is quite small, being of order 5% or less. A possible reason for this difference is the neglect of energy terms arising from the fact that the anions in crystals with the rutile structure are permanently polarized, as discussed by Yamaka & Narita (1966) in connection with their calculation of electric field gradients in TiO_2.

The possibility of the existence of such a polarization can be seen from the fact that the anions in a rutile structure occupy sites at the intersection of only two perpendicular reflection planes. The absence of the third, and mutually perpendicular, reflection plane allows for the presence of an electric field at the site which polarizes the anion.

In the dipole approximation, the extra lattice energy can be considered to result from the electric potential produced at each ion site by the anion dipoles. Mathematically, this energy is the summation over all ions $\frac{1}{2}\sum_i q_i V_i$, where q_i is the ionic charge and V_i is the dipolar potential at the ion site. The factor $\frac{1}{2}$ and the absence of the dipole–dipole term account for the energy required to form the dipoles.

This correction has been calculated for TiO_2. First, lattice potentials due to Ti^{4+} and O^{2-} ions were calculated at various sites in the unit cell by a direct summation using a point ion model and a Univac 1108 computer. Shells of unit cells were constructed around the central cell in a symmetric way by the computer until convergence of the potential occurred. Ten shells were sufficient to bring computed potentials to within 0·02% of their convergent values. The lattice parameters used are those cited by Hurlen (1959): $a=4{\cdot}594$, $c=2{\cdot}959$ Å and $x=0{\cdot}3054$. These parameters yield ion-site potentials of $-51{\cdot}99$ volts at titanium sites and $+18{\cdot}61$ volts at oxygen sites. Using these potentials and Baur's average Ti–O distance of 1·961 Å, the Madelung constant was determined to be 4·807. This compares favorably with Baur's result 4·810.

In order to calculate the dipole moment of the oxygen ions, the polarizing fields due to the point ions and the dipoles themselves were considered in a self-consistent manner. By calculating the ionic potential at points 0·05 Å on each side of an oxygen site, the electric field E_i at the site due to point ions was determined to be $2{\cdot}82\times10^{10}$ volts.m^{-1}. This is directed along the line of intersection of the two reflection planes, where the positive sense is toward the nearest titanium ion in the same basal plane.

The polarizing field due to the dipoles themselves was calculated by first assigning to each oxygen ion a unit dipole moment $P_u=(e).(1{\cdot}0\text{ Å})$ in the direction of E_i. By calculating the potential due to these unit dipoles at points 0·05 Å on each side of an oxygen ion site, an electric field E_d was determined to be $2{\cdot}38\times10^{10}$ volts.m^{-1}. The actual dipole moment P of the oxygen ions was then calculated from the equation

$$P=AP_u=\alpha(E_i+AE_d)\,,$$

where α is the polarizability of an oxygen ion. The value of α used was that determined experimentally by Tessman, Kahn & Shockley (1953), $\alpha=2{\cdot}4\times10^{-24}$ cm^3. The solution for A is 0·778, thus giving the actual oxygen-ion dipole moment $(e).(0{\cdot}778\text{ Å})$.

The permanent oxygen dipoles produce potentials of $-0{\cdot}489$ volt and $+0{\cdot}611$ volt at the titanium and oxygen sites respectively, and these result in a contribution of 50·8 kcal.mol^{-1} to the lattice energy. This extra term increases the theoretical lattice energy to 2480 kcal.mol^{-1}, which is to be compared with the experimental value of 2900 ± 70 kcal.mol^{-1}. The difference between the two remains large after consideration of the dipole correction, thus preserving Baur's view that TiO_2 is non-heteropolar.

The dipole correction in the case of TiO_2 is about 2%. Insofar as all rutile structures are of similar dimensions, the dipole correction for the fluorides can be estimated. The polarizability of the fluorine ion is about 27% that of O^{2-}, and the ionic charges in the fluorides are one-half those

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in TiO_2. These factors cause the induced dipole mcment of the fluorine ions to be an order of magnitude less than that of the oxygen ions in TiO_2. This leads to an energy correction of about 0·4% in the cases of the fluorides, which is not enough to bring the theoretical and experimental results into agreement.

In conclusion it should be emphasized that these results are at best approximate owing to the fact that the electric field varies both in magnitude and direction over the diameter of an oxygen ion in TiO_2. It has been assumed here that the polarizing field is that at the center of the ion.

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A simple method for finding the plane of a planar, or partly planar, molecule.

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The plane of a molecule may be found simply by calculating the equations of all planes passing through the origin and two of the peaks in Patterson space, and the distances of all other peaks from each such plane. From the results, the approximate equation of the molecular plane will be obvious, and may be improved by least-squares techniques. This method has the advantage over the $I(\theta,\varphi)$ method that it requires only a small computer and little computer time.

A method of determining the orientation of the planar part of a molecule has been described by Tollin & Cochran (1964). In this method a disc is placed with its centre at the origin of Patterson space, its orientation being determined in terms of the spherical polar angles θ and φ which define the normal to the plane of the disc. The sum of the Patterson function over the disc, $I(\theta,\varphi)$, is calculated as the disc is rotated, and the orientation of the disc when this sum is a maximum is taken to correspond to the plane of the molecule. In this paper a simpler method for determining the molecular plane is described.

A list is made of all peaks in Patterson space which lie within such a distance from the origin as to include all intramolecular vectors. The equations of all planes passing through the origin and two of these peaks, and the distances of all other peaks from each such plane, are calculated. Many of the resulting planes will have approximately the same equation and will have many peaks situated close to them. The best-fit plane through all such peaks, defined as that plane for which the sum of the squares of the distances from the peaks to the plane is a minimum, is then calculated. This should be a good estimate of the plane of the molecule.

This method was used to determine the molecular plane of $\alpha\gamma$-dimethyltetronic acid, $C_6H_7O_3$, which was believed to be almost wholly planar. The space group is $P2_1/c$, and the cell dimensions are $a=6\cdot66$, $b=14\cdot18$, $c=6\cdot58$ Å, $\beta=100\cdot3°$. The molecular plane was found by the method described to be

$$0\cdot18x+0\cdot98y+0\cdot00z=0\,.$$

The equation obtained from the $I(\theta,\varphi)$ calculation was

$$0\cdot275x+0\cdot960y+0\cdot004z=0\,,$$

and the final equation of the plane obtained after determination of the structure was

$$0\cdot284x+0\cdot958y-0\cdot038z=0\,.$$

Comparison of the equations of the two planes initially obtained with the equation of the plane in the final structure shows that the method of Tollin & Cochran gave a slightly better estimate of the molecular plane. The plane obtained from the $I(\theta,\varphi)$ calculation is less than 1° away from the final plane while the other plane was 4° off.

The main source of error in the determination of the molecular plane by the method described is probably due to including peaks which, although they lie near to the plane of the molecule, are not due to vectors between atoms in the planar parts of the molecule. If the molecule is large and only partly planar, there may be a number of such peaks. These peaks will also contribute to the $I(\theta,\varphi)$ calculations, but should not alter the position of the maximum. Further, since the latter method involves the summation of the Patterson function over a plane, the peaks are effectively weighted according to their height. The adoption of a weighting scheme may improve the method described here.

There is also the difficulty of deciding where the centre of a Patterson peak is situated, and whether the peak is a single or multiple one.

The advantage of the method is that it involves a very short and simple computer program while the $I(\theta,\varphi)$ calculation requires a complicated program run on a computer having a large storage capacity, even though the full Patterson function does not need to be calculated. Where access to a large computer is not available, and where computer time is at a premium, the method described will yield a starting point for a structure determination very quickly. It might even be possible in some cases to obtain the approximate molecular plane by visual inspection of the Patterson function, after which the least-squares plane may be calculated for the peaks near this plane, no computer being necessary.

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