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Thermal Vibrations of Atoms and Molecules in Crystals

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NO crystal structure has yet been adequately determined. This applies particularly to the crystal structures of small organic molecules, in spite of the many papers that have appeared about some of them.

A proper determination would include exact mean positions of all atoms, including hydrogen; a study of the electron distribution of the atoms in a state of rest; a knowledge of the zero-point motions and of the thermal vibrations of all atoms, analyzed with respect to translations and oscillations of the molecules as a whole and of the atoms relatively to each other within the molecule; the distribution of these with respect to amplitude and frequency, at various temperatures; a study of imperfections, unavoidable or deliberately introduced; and of surface modifications of structure.

Now that high-speed computing facilities are available, the principal bottleneck in obtaining much of this information appears to be the difficulty of getting really reliable and precise experimental data on which to work. When we first began a concerted study of thermal vibrations in such structures as hexamethylene tetramine (cubic), urea, pentaerythritol, di-para-xylylene (tetragonal), benzil (trigonal), anthracene, naphthalene (monoclinic), hexamethylbenzene (triclinic), and also in compounds containing heavy atoms, we hopefully supposed that it would be possible to regard these problems as providing suitable work for postgraduate students having had little actual experience in making accurate measurements of diffraction geometry and intensity. We have been sadly disillusioned. With care, and given time, students can obtain measurements of diffraction intensity at any given temperature, having an internal consistency of about 10%. This is not good enough because, to within this degree of reliability, many combinations of slightly differing coordinates and isotropic or anisotropic amplitudes of vibration can be found to give agreement between observed and calculated data, especially if only one diffraction technique is used. This point is elaborated in our papers on urea.[1]

We feel that it is, in fact, essential to use more than one diffraction technique and to regard any results as provisional that have not been confirmed by at least one other diffraction technique. The literature has recently shown that data for simple structures obtained by x-ray, electron, and neutron diffraction methods, all claiming considerable accuracy, do not agree, or only agree to just within the limits of experimental error. It seems advisable in such circumstances for the individual investigators concerned to get together and to discuss their methods in detail in order to see where the discrepancies may have arisen.

In our laboratory we are interested in the following methods.

(1) We study the structure of a given substance in single crystal form by x-ray diffraction methods at room temperatures and at a low temperature (boiling liquid nitrogen or, in the future, liquid hydrogen). This assumes that the structure is known to a fair degree of approximation, and involves the successive refinement of coordinates of all atoms (including hydrogen), and of the vibration amplitudes along the axes of the vibration ellipsoid (in a specified orientation) for each atom. This is done either by least-squares approximations, in which case the refinement of coordinates and vibration amplitudes takes place alternately, by steps, or by difference Fouriers, where the refinement of both is carried out simultaneously.

Agreement between calculated and observed structure factors is only significant, however, if the observed structure factors are not only derived from accurately determined intensities, but also have been properly corrected for such effects as extinction, dispersion, and absorption. Extinction may be allowed for to a certain extent by using several crystals, or by shock heat treatment, but we hope to study and to obtain a first-order correction for both primary and secondary extinction by the use of polarized x-rays, as suggested by S. Chandrasekhar.[2] Dispersion and absorption are less important for molecules containing light atoms only, but need to be considered especially if heavy atoms are present or long wavelengths are used. It is often forgotten, for example, that dispersion changes not only the amplitude but also the phase of a reflexion, and eliminates the center of symmetry in an otherwise centrosymmetric structure. Figure 1 shows that the effects of dispersion and/or absorption on the atomic scattering factor may be so disguised by a scaling process as to falsify the determination of thermal vibration effects.

While this could only happen in the form shown for a really simple ionic or atomic structure, the same principle applies to molecular structures. Referring now, however, to the case of a diatomic cubic structure, recent work by Jack and Wachtel[3] on $Cs_{3+x}Sb_{1-x}$ has

[1] R. E. Gilbert and K. Lonsdale, Acta Cryst. **9**, 697 (1956); H. J. Grenville-Wells, *ibid.* **9**, 709 (1956).

[2] S. Chandrasekhar, Acta Cryst. **9**, 954 (1956).

[3] K. H. Jack and M. M. Wachtel, Proc. Roy. Soc. (London) **A239**, 46 (1957).

shown how important it is to allow for individual thermal vibrations for the separate atoms. The structure is of a partially random sodium thallide type, but a complete series of x-ray superlattice reflections with h, k, and l all odd appear due, not to shifts of the atoms from special positions, but to the widely different values of the vibration amplitudes ($(\bar{u}^2)^{\frac{1}{2}}=0.52$A for Cs, 0.25A for Sb, at 291°K). The variations of F^R/F^T (R=rest, T=thermally vibrating) for different hkl are striking, both in the differences of numerical values and of sign shown, and in showing the effect of dispersion. The results shown in Table I have been privately communicated to me by Jack.

It is interesting to notice that whereas the usual interpretation of $F^R/F^T=1$ would be that the effect of atomic vibration on this particular spectrum is negligible, yet $F^R/F^T=-1$ may correspond to a large vibration effect, especially if F is itself not very small. The implications of this in terms of comparisons of diffraction intensities at different temperatures is obvious. If measurements were only taken at two temperatures, it would have been possible for the ratio F^R/F^T to have passed through the value infinity and then to lead to no apparent change of intensity at the particular temperatures chosen.

In the case of a supposedly disordered cubic structure, any variation in the value of F^R/F^T from one reflection to another will indicate that a degree of order must exist, with differing vibration amplitudes for the different atoms. It seems clear that this must be what occurs in the case of α brass.[4]

A theoretical estimate of zero-point energy can be made in the case of very simple structures, and early work by James, Brindley, and others[5] showed that better agreement between calculated and observed structure factors was obtained by the inclusion of zero-point energy.

No such estimate can be made with any degree of accuracy for even the simplest molecular structure, and

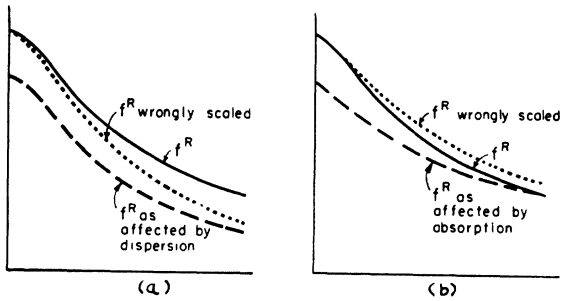

FIG. 1. Assuming F_{obs} is scaled to agree with F_{calc}, and ignoring the effect of dispersion and absorption, (a) the B factor may appear larger than it really is or (b) the B factor may appear smaller than it really is, or even negative.

[4] K. Lonsdale and H. J. Grenville-Wells, Nature **177**, 986 (1956).
[5] I. Waller and R. W. James, Proc. Roy Soc. (London) **A117**, 214 (1927); R. W. James and G. W. Brindley, *ibid.* **121**, 155 (1928); James, Brindley, and Wood, *ibid.* **125**, 401 (1929).

TABLE I.

hkl	F^R/F^T without dispersion	F^R/F^T with dispersion
111	+2.75	+2.12
220	+1.56	+1.15
311	−1.02	−0.75
400	+1.43	+1.31
331	−0.49	−0.40
800	+2.96	+2.72
733	−0.21	−0.19
880	+6.28	+5.76
971	−0.24	−0.24

therefore some attempt needs to be made by experimental methods to distinguish thermal vibration effects from zero-point motion and from anisotropy of electron distribution in the atoms at rest. This can be done by making measurements at different temperatures. A really accurate structure analysis at a low temperature as well as at room temperature, in spite of the difficulties introduced by termination of series errors, does enable genuine thermal vibrations to be sorted out from other effects. In principle, this method is greatly facilitated by the use of absolute intensity data.

(2) Measurements of the variation of the diffraction intensities from a number of planes, at several temperatures, enable an independent estimate of temperature factors to be made. If a curve is drawn for each diffraction spectrum and the trend of data at low temperatures is sufficiently clear-cut for extrapolation to 0°K to be possible, then a measure of F^0/F^T is possible for each spectrum at any given temperature T. Method (1) has given F^{R_1}/F^{T_1} and F^{R_2}/F^{T_2} at two specific temperatures, by means of really accurate and detailed analyses involving large numbers of reflections. These analyses tell us how the structure itself, apart from any atomic vibrations, is changing with temperature, since F^{R_1} and F^{R_2} refer to the "rest" structures, using spherical atomic scattering factors, at each temperature. F^0, on the other hand, refers to a structure at 0°K which is not at rest, but subject to zero-point motion, and in which the atoms may not be spherical, but may have an anisotropic electron distribution. The atomic coordinates and unit cell size at 0°K will be obtainable by a rather simple extrapolation from the crystal structure analysis at the lowest available temperature.

Provided that the change in structure is not large, the curve of F^0/F^T for a series of diffraction spectra and a given temperature T should be nearly parallel to the corresponding curve for F^R/F^T, but it will be separated from it by a gap which is a measure of the zero-point motion and the bonding anisotropy, as these affect the structure factor for each spectrum.

For any given structure it is, however, important to make sure that the effect of change in structure on the Bragg angle and hence on all factors dependent on the Bragg angle, has been adequately allowed for.

(3) In the process of determining the structure at

different temperatures it is a simple matter to plot the thermal expansions in different directions. This has been done by previous workers (Robertson, Ubbelohde, Woodward, and others[6]) but what we would like to see is a systematic collection of this information for each structure at the time of its structure analysis. It seems certain that this could provide a useful auxiliary method of distinguishing vibrations which vary with temperature from those which do not. In the case of tetragonal crystals, such as urea, pentaerythritol, and di-para-xylylene, the relationship between amplitudes of vibration and thermal expansion is direct and obvious, but with monoclinic structures such as anthracene or naphthalene the relationship may not be so direct, but it exists.

The plotting of sections of the expansion surface is also an excellent test of the accuracy of measurement of crystal geometry at different temperatures, since these sections will be smooth curves.

(4) It is also a very simple matter, while x-ray photographs are being taken, to collect a series of well-exposed cylindrical Laue photographs or precession photographs, from which a complete picture of the *diffuse* scattering in reciprocal space can be built up. It may not yet be possible to interpret this wealth of information in more than a qualitative or semi-quantitative way, but it is important to obtain the data because this is one way in which the distribution of vibrations among different frequencies could be examined.

The general relationship of the diffuse scattering surfaces in reciprocal space to the thermal expansion surfaces has been noted, for example, in oxalic acid dihydrate[7] and general experience has shown us that an obvious relationship can often be seen between the streaks and sheets of diffuse scattering and the known orientation and movements of molecules. Changes in distribution of thermal wavelengths with temperature may be followed either by photographic or counter methods. These changes have been followed in detail using lead single crystals.[8]

(5) We have not yet made any measurements on crystals in which isotope substitution has been carried out. In (1) to (4) above, the experiments described can all be made on crystals of the same substance, with very little extra trouble. There seems little doubt, however, that similar data obtained either with deuterated compounds or perhaps with a change of heavy atom (but not too heavy) could, by changing the conditions in a known way, give additional information which, even if it could not be thoroughly understood, might build up the evidence to a point where the different parts of the jigsaw would tend to fall into place.

(6) Any anisotropic physical property of the crystal that changes with change in orientation of the molecule or that changes with relative change of position of neighboring molecules can, in principle, be used to obtain information about molecular movements. For example, the diamagnetic susceptibilities along the principal magnetic directions in organic crystals do change slightly with temperature although the mean diamagnetic susceptibility seems not to change.[9] Miss Leela, in my laboratory, has also made such measurements on some of the substances mentioned above. Where no change in mean molecular orientation with temperature is possible, as in urea, then any change of diamagnetic anisotropy can be interpreted in terms of molecular librations. The huge temperature variation for graphite is mainly due to the Landau diamagnetism of free electrons and holes, but this effect decreases fast with molecular size and is negligible, for example, for anthracene, for which the diamagnetic anisotropy is due entirely to the π electrons. The interpretation of changes with temperature of diamagnetic anisotropy of molecules where change of orientation is possible, depends entirely upon an accurate knowledge of structure in a state of rest, at the temperature in question. Given such information, the magnetic data can supply corroborative evidence concerning the molecular vibrations. If any discrepancy still exists between the observed diamagnetic anisotropy changes and those to be expected from the molecular vibrations, then it may well be worthwhile to consider whether actual changes with temperature in the quantum-mechanical state of the molecule take place.

[6] J. M. Robertson and A. R. Ubbelohde, Proc. Roy. Soc. (London) **A170**, 222 (1939); A. R. Ubbelohde and I. Woodward, *ibid.* **181**, 415 (1943).

[7] J. L. Amoros and M. L. Canut, Publs. dept. crist. mineral. Univ. Barcelona **2**, 155 (1956).

[8] See, for example, L. Cartz, Proc. Phys. Soc. (London) **B68**, 951 (1955).

[9] J. Hooran, Thèse, Paris (1954); Ann. chim. (to be published); quoted by N. Lumbroso-Bader, Ann. chim. **1**, 687 (1956).