

The New Crystallography.

By F. I. G. RAWLINS.

THE attraction which the study of crystals has always exerted, not only upon the scientific worker but also upon a wider circle, is in no danger of abating. The time is perhaps appropriate to discuss a number of developments which have come about during, roughly, the last five years. So far as the crystalline state itself is concerned, the chief change has been one of classification; it is not necessarily the crystal system which determines much of our present-day knowledge, but rather the atomic environment. Thus, in rock salt, each atom (or more strictly, ion) of sodium is surrounded by six ions of chlorine at the corners of an octahedron, and conversely. From the experimental point of view, this advance must be placed to the credit of the X-ray workers; it has only comparatively recently been recognised, however, that upon the structures thus established it was possible to build up a systematic chemistry of the solid state, based upon the conceptions of environment, ionic size, and ionic deformability.

It has come about that a considerable part of the subject of crystallography is concerned with the question: Given the structures of a large and increasing number of elements and compounds, how much can be deduced about their physical and chemical properties? And again, one asks what kind of experiment is most likely to provide this information, and whether it is essential to work with crystals at all in some instances. These queries are easily seen to reduce to this: whether it is desired to know something about the crystalline lattice, or whether it is the components of the lattice that are the more important. Research of the former kind obviously needs actual crystals, whereas the latter may be able to make some progress in states of matter wherein lattices, as ordinarily understood, do not exist: for example, solutions and even gases. Clearly, the new crystallography will trespass upon the preserves of many neighbouring sciences.

The Union of Ions into Crystals.—From a logical point of view, it is not altogether fortunate that so much attention has been given for so many years to the morphology of crystals as such. A more fundamental way to proceed would be to consider a free atom of an element A at some distance from a free atom of some other element X , and to follow the course of events in which all the A 's and all the X 's are bound so that the assemblage $\Sigma[A, X]$ is in equilibrium, at a temperature such that the components A and X are constrained to fulfil certain definite geometrical conditions with respect to each other. Stability will ensue for that particular configuration of $\Sigma[A, X]$, say $S[A, X]$, for which the energy is a minimum. In other words, the arrangement $S[A, X]$ represents a crystal.

This view has led to some very interesting results in a series of experiments upon the alkali halides. The ionic refractivity, which depends upon the deformability already mentioned, can be measured in the free state, R (free ions), and in the crystalline

state, R (solid). Now, cations and anions behave very differently in the presence of each other. Anions are consolidated, or rendered more rigid, by neighbouring cations, because in addition to the attraction of the nucleus of the anion for its own electrons, there is added that of the positive cation. A similar argument shows that just the reverse holds for a cation under the influence of an anion—the distortion or deformability increases. Hence, in the former case the refractivity decreases, and in the latter it rises. Thus the union of ions to form a crystal will bring about a net decrease in refractivity when the consolidating effect of cations upon anions preponderates over the loosening effect of the anions upon the cations, and vice versa. For most of the alkali halides the difference R (solid) – R (free ions) is negative, which corresponds to a net consolidation when the crystal is formed out of the appropriate free ions. Only for potassium and rubidium fluorides (KF and RbF), in which a large ion is paired with a small ion, is a net loosening indicated. A balance is approximately obtained for sodium fluoride (NaF) and rubidium chloride ($RbCl$): the experimental accuracy is not high enough to detect very small differences in the refractivities.

In aqueous solution the refractivity is found to vary with concentration in a manner which suggests that at high concentrations the ions approach each other nearly as closely as in the crystal lattice; they are in direct contact, with no intervening water molecules. Other examples of relationships between crystals and solutions will occur later; they have been fairly extensively studied by spectroscopic methods.

Crystal Thermodynamics.—Strictly, thermodynamic reasoning is independent of a mechanism, and in this sense its application to crystal lattices and the particles composing them is not very obvious. Nevertheless, an extension of its proverbial boundaries has extended our grasp of the energetics of the solid state. To show how this has happened, two examples, characteristic of the most modern work, will be discussed. In the first, one is dealing with a sub-lattice property, and in the second, with a lattice property. Consideration in this particular order will serve to stress the general outlook of this article; the units composing a crystal are, from this aspect, of prior importance to the particular way in which they may be grouped.

The quantum theory, applied to gaseous molecules, has been fruitful in unravelling the complexities of rotational and vibrational motion. The latter has long been recognised to be characteristic of the solid state also, but it is only very recently that the possibility of molecular rotations in crystals has been seriously considered. The work is for the most part theoretical, and based upon suitable applications of the wave mechanics to diatomic molecules. The wave equation appears in the form of Mathieu's equation, and the corresponding energy levels are generally readily deducible.

Analysis shows that two extreme cases may be discerned; one in which the energy equations are those of the quantised harmonic oscillator, while the other approaches the value for the rotator. The next step is to obtain a discriminant, in terms of measurable quantities, for the transition between oscillational and rotational motion. The inequalities

$$n + 1 < \beta v / 4\theta \text{ (oscillational),}$$

and

$$n + 1 > \beta v / 4\theta \text{ (rotational),}$$

provide, on certain assumptions, the criterion desired, for the quantum state n and frequency ν . The factor θ depends upon the moment of inertia, which is readily forthcoming from spectral data, while β is a constant. Another, and in some respects a simpler analysis, demonstrates that rotation may be expected at temperatures greater than $2V/k$, and oscillation for values less than this fraction (V is a characteristic quantity in the potential function for the particular molecule considered, and k is Boltzmann's constant). The probability that a molecule will rotate is capable of approximate calculation, yielding $P = e^{-2V/kT}$, where T is the temperature.

The expressions in terms of n and θ can conveniently be combined into the equation $n_0 + 1 = \beta v / 4\theta$, where n_0 is the particular value of n , which is on the borderline between the rotational and vibrational states. For hydrogen (H_2), with its small moment of inertia, $n_0 + 1 \sim 0.4$, whereas for iodine (I_2) $n_0 + 1 \sim 350$. From these figures, it follows that the molecules in solid hydrogen are rotating even in the lowest quantum states, whereas in iodine no molecules are rotating in the crystal, since melting occurs for $n \sim 12$.

The ammonium salts provide an interesting example of substances for which the transition from rotation to vibration may be expected to set in well within the solid range. A temperature of about 240° absolute is indicated by the theory. Observations of the heat capacity as a function of temperature have shown that in a number of substances there is a finite range of temperature over which the relative numbers of molecules in either state is undergoing a progressive change.

The second contribution, already alluded to, concerns the form of the specific heat curve (particularly at low temperatures) as a function of the crystal symmetry of the substance. If one assumes that the usual Debye equation represents the facts for the cubic system, then, as materials of decreasing symmetry are examined, instead of following the 'ideal' curve (convex upwards), an approximately straight line results. The sequence is well seen in the series zinc sulphide (cubic), zinc oxide (hexagonal), cupric oxide (triclinic). The importance of this effect is that the specific heat is influenced by the atomic environment, a typical lattice property.

Crystal Spectra.—As in the thermodynamical matters already discussed, it is convenient to divide crystal spectra into two main classes, those of ionic (or even sub-ionic) origin, and those for which the lattice, or at least parts of the complete lattice, are responsible. In dealing with the former,

one is tempted to make a yet finer distinction between the types of spectra in which ions, or groups of ions, are concerned (in contradistinction to the swinging of large portions of the whole lattice), and phenomena which have their seat within the ion itself: that is, transitions of an electronic nature. Spectra arising from these three causes may be expected to appear at increasing wave-length as the mass of the unit concerned increases. Thus, sub-ionic (electronic) absorption spectra in crystals may occur in the visible region, and are closely connected with the nature of colour. Inter-ionic spectra are found in the near infra-red (between about 1μ and 30μ); lattice spectra are revealed at a wave-length some ten times greater, and are usually detected by the method of residual rays, or some system involving focal isolation. Oscillations of approximately these frequencies are those encountered in the theory of specific heats already mentioned.

In electronic crystal spectra, restricted in the main to salts of the rare earths and those of the transitional elements, one is confronted with a problem of great complexity, intimately connected with electronic levels and the magnetic properties of ions with incomplete electronic shells. There is little doubt that the sharpness of the bands in the visible region is attributable to the high electrostatic shielding and weak coupling between the electrons belonging to neighbouring ions. Information of value to chemists may well be obtained by studies of this kind.

Somewhat similar investigations have produced some illuminating results when the absorption spectrum of an ionic group like MnO_4 is examined in a crystal and in solution. The effect of dissolving, say, potassium permanganate, in water is to slow down the oscillations characteristic of the group, owing to the outward pull of a solvent of high dielectric constant ($=80$): solution in ethyl acetate (D.C. = 6) allows the MnO_4 group to contract to almost the same dimensions as it has in the crystal lattice of potassium permanganate. In other words, the surrounding molecules of ethyl acetate have much the same effect upon the MnO_4 tetrahedron as the ions of potassium in the solid state.

It is natural to infer from this that much might be gained by careful study of the dielectric constants of crystals, especially at temperatures immediately below the melting point. Much the same applies to observations of absorption spectra in crystals at different temperatures. A promising start has already been made at the low temperature end, but the technical difficulties are great, and the results will need much skill to interpret.

No attempt has been made to discuss the Raman effect in relation to crystal physics and crystal chemistry: already the literature is voluminous, and the significance of some of the results by no means clear. The method is certainly of great value. Statistical mechanics may be expected to play a considerable part in the future development of the new crystallography; in fact, all the resources of modern science can contribute something to our knowledge of the solid state.