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Quantum theory and crystal physics*

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1. Introduction

The physics of the twentieth century differs fundamentally from the physics of the nineteenth mainly because of two theories known respectively as the Quantum Theory and the Theory of Relativity which form an integral part of its scheme of thought. It is these two theories that have enabled a far deeper understanding of the nature of the physical world to be attained than was possible at the end of the last century. One must here acknowledge the work of Albert Einstein who played the leading role in the development of both of these theories. His publications during the first two decades of the present century bear on every page the imprint of a powerful and penetrating intellect. Even after this lapse of years, the physicist of today will find the study of those papers a profitable and stimulating experience. Indeed, a good deal of what I have to say in this address only reflects the results of such a study in relation to the fundamental problems of the crystalline state of matter—a subject which has deeply interested me for several years past.

2. Origin of the quantum theory

The quantum theory arose from the attempt to explain the characters of the radiation which emerges from the window of an enclosed furnace heated to high temperatures. As is well known, the total intensity of such radiation increases rapidly with rise of temperature of the furnace. Simultaneously, there is a shift of the spectral maximum of intensity towards higher frequencies, as is indeed evident from the progressive change in colour of the radiation. Thermodynamic considerations indicate that this shift should occur in such a manner that the spectral frequency at the point of maximum intensity should be directly proportional to the absolute temperature of the furnace. Quantitative measurements confirm that this is the case and show that the changes in the intensity as well as in the spectral character of the radiation with rise of temperature agree

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with a formula for the spectral intensity in which the cube of the spectral frequency appears multiplied by an exponential function of a type made familiar by Boltzmann's well known principle. The argument of the exponential function is negative and has as its numerator the spectral frequency multiplied by one universal constant and as its denominator the absolute temperature multiplied by another universal constant. A small but important modification secures a much more satisfactory agreement between the formula and the facts of observation. In the modified expression, the exponential has the same argument with a positive sign and now appears in the denominator with unity subtracted from it. This is the celebrated Planck formula except for a multiplying numerical factor.

3. Einstein's derivation of the Planck formula

Einstein gave a physical interpretation of the Planck formula and also showed how the formula could be derived on the basis of simple physical considerations. He interpreted the formula to mean that radiation of all frequencies is emitted and absorbed by material bodies in discrete quanta of energy proportional to their respective frequencies. He also showed that the radiation formula follows very naturally if we assume that the energy of the material particle which emits the radiation is itself quantised, in other words, its energy of vibration alters by successive steps, each of which is equal to the quantum of radiation energy which is emitted in the process.

A more complete and logically satisfying derivation of the Planck radiation formula was given by Einstein ten years later, viz., in 1917. In that paper, the notion of probability which in the quantum theory replaces the determination of the older physics finds a prominent place. Instead of assuming the radiator to be a harmonic oscillator as in his paper of 1907, Einstein dealt with the most general case of an oscillator which has a number of discrete energy levels. The probability of its being present in any one of them is expressed by the product of the inherent statistical weight characteristic of the level multiplied by the appropriate thermodynamic probability factor. The latter takes the form of an exponential function with a negative argument equal to the energy of the state divided by the product of the absolute temperature and the Boltzmann constant. Einstein then considers the probability of three different kinds of elementary processes occurring in any given small time interval. The first is a spontaneous transition from the higher to a lower state of energy with emission of radiation as contemplated in Bohr's theory of spectra; the second is a transition of the same nature but now induced by the presence of an external radiation field; the third is a transition from the lower to the higher energy state also induced by the external field. The probabilities of the two latter transitions are taken as proportional to the energy density in the surrounding radiation field. A transfer of energy from the oscillator to the field and an absorption of energy from the field by the oscillator are involved respectively in the two processes. In a steady state of affairs, the probabilities of transition in the two opposite directions must necessarily balance each other. These considerations lead at once to the Planck radiation formula.

4. The crystal as an assembly of oscillators

The foregoing exposition of Einstein's original ideas is intended to furnish a theoretical background for a consideration of the fundamental properties of the solid state which is the subject of the present address. Elementary processes closely analogous to those contemplated in Einstein's paper of 1917 successfully describe the phenomena actually observed when a beam of monochromatic light traverses a crystal and the light diffused in its interior is examined spectroscopically. We observe in the spectrum of the scattered light sharply defined lines with frequencies both higher and lower than that of the incident radiation. The ratio of the intensities of each such pair of lines having equal spectral displacements in opposite directions is found to be expressed correctly by a Boltzmann factor corresponding to the change of frequency multiplied by Planck's constant, this again being multiplied by the fourth power of the ratio of the two spectral frequencies. These facts indicate that the displaced frequencies arise from transitions from a higher to a lower energy state and vice versa induced in the elementary oscillators comprised in the crystal by the incident radiation. We are thus naturally led to regard the crystal as an assembly of a great number of oscillators which form a system in thermodynamic equilibrium. The thermal energy of the crystal may then be equated to the sum of the thermal energies of all the oscillators of the different sorts of which it is composed.

It is evident from what has just been stated that the specific heats of crystals stand in the closest relation to their spectroscopic properties. The first step in the theoretical evaluation of the thermal energy of the crystal is accordingly to identify and enumerate the oscillators of which it is composed and to discover and specify the energy states which they can occupy.

5. The oscillators and their energy levels

To begin with, we may provisionally identify the oscillators with whose behaviour we are concerned with the groups of atoms present in the unit cells of the crystal structure. To discover the energy levels which these oscillators can occupy, we may, at least in regard to the infra-red or vibrational levels, adopt the same procedure as that which has proved itself abundantly successful in the field of molecular spectroscopy. As is well known, that procedure consists in determining and enumerating the different possible modes of vibration in each one of which the atoms all vibrate with the same frequency and in the same or opposite phases.

In endeavouring to carry through the procedure indicated above, the difficulty immediately presents itself that the group of atoms present in any one unit cell of the crystal structure is not isolated but forms a connected system with the groups of atoms in the surrounding cells and these latter again are connected with groups of atoms further out and so forth. The mathematical and physical difficulties which present themselves by virtue of these inter-connections disappear when we make use of the fundamental property of crystal structure, viz., that it comes into coincidence with itself following a unit translation along any one of its three axes. Hence any normal mode of vibration should also possess the same property viz., it remains a normal mode following a unit translation of the crystal. This requirement immediately enables us to determine and enumerate the normal modes in the most general case of a crystal consisting of several interpenetrating Bravais lattices of equivalent atoms. It emerges that the normal modes are divisible into two classes; in the first class, the amplitudes as well as the phases of oscillation of equivalent atoms in adjoining cells of the lattice structure are identical, while in the second class of normal modes the amplitudes of equivalent atoms are the same but the phases are reversed along one or two or all three of the axes of the lattice. If the crystal consists of p interpenetrating Bravais lattices, there are $(3p-3)$ normal modes of the first class and $21p$ modes of the second class.

Thus the result emerges that the vibrational energy levels of a crystal form a sharply defined set in much the same manner as the vibrational energy levels in the spectra of molecules. But this result would necessarily be modified when the effects of anharmonicity and the interactions of the different normal modes with each other are taken into consideration.

6. The spectroscopic behaviour of crystals

The theoretical results stated above are in complete agreement with the actual spectroscopic behaviour of crystals in the infra-red region of frequencies as revealed by diverse techniques of observation in appropriate physical conditions. For example, they furnish an immediate explanation of the spectroscopic effects exhibited by crystals in the scattering of monochromatic light as mentioned earlier. In some cases the energy levels are shown by the spectral shifts to exhibit a lack of sharpness. That this arises from the disturbing effects of anharmonicity is demonstrated by cooling down the crystal to liquid-air temperature. The energy levels then become perfectly sharp, as is to be expected. We need not dilate here upon the different techniques of spectroscopic observation which are available only in particular cases. Mention should be made, however, of the very general method of observing the energy levels in crystals by the techniques of infra-red absorption. These latter have been greatly improved of recent years and the results obtained with such improved techniques completely confirm the theoretical findings stated above.

A feature of special interest to which reference may be made here is in respect of the possibility of observing the $21p$ normal modes of the second class in which the phases of oscillation are opposed in adjoining cells of the crystal structure. It is to be expected that by reason of such opposition of phase these modes would be precluded from observation by any of the available methods of spectroscopic study. Fortunately, however, and for reasons which I shall not here dilate upon, this is not invariably so. The normal modes of the second class are actually accessible to observation in several cases and they then manifest themselves as discrete and sharply defined lines in the spectra, provided the effects of anharmonicity are either absent or else are suppressed by the use of adequately low temperatures. Their appearance is one of the most striking vindications of the correctness of the present theoretical approach.

7. The specific heats of crystals

Regarding a crystal as an assembly of an immense number of oscillators in thermodynamic equilibrium, the evaluation of its thermal energy as a function of the temperature reduces itself to the problem of classifying and enumerating the different sorts of oscillators comprised in it and determining the scheme of energy levels for the oscillators of each sort. An application of Boltzmann's principle then enables us to evaluate the average energy of an oscillator of that sort, and multiplying it by the number of such oscillators we obtain a sum total; the addition of the sums thus found for the different sets of oscillators gives the total thermal energy of the crystal. By differentiating this total with respect to the temperature, we obtain the specific heat of the crystal.

As already stated, we have $(3p-3)$ normal modes of vibration of the first kind and $21p$ normal modes of the second kind. Thus, we have $(24p-3)$ modes and frequencies in all and these have equal statistical weight. They may be regarded as the internal modes of vibration of the $8p$ atoms contained in a volume element of the crystal whose dimensions are twice as large in each direction as the unit cell of the crystal structure. The three omitted degrees of freedom represent the translatory movements of these groups of $8p$ atoms each. If we leave the latter aside for a moment and also neglect the effects of anharmonicity, the specific heat of a crystal may be expressed very simply as the sum of $(24p-3)$ Einstein functions, each involving its own characteristic frequency; the total number of oscillators which contribute is the number of groups of $8p$ atoms each comprised in the crystal. To this sum must be added the contribution to the specific heat arising from the oscillations inside the crystal which are attributable to the translatory movements of these groups of 8*p* atoms each. In a paper which has appeared in the October issue of the *Proceedings* of the Academy, it has been shown how the latter contribution may be rigorously evaluated. The argument by which this is affected may be very simply stated. The translatory movements of the groups of 8*p* atoms each give rise to oscillatory movements in volume elements which comprise a still larger number of atoms. By taking a succession of volume elements of different sizes and taking note of the circumstance that the lower limit of frequencies of vibration thus arising would diminish in proportion to the increasing dimensions of the volume element, the spectral distribution of frequencies follows immediately. Their contribution to the thermal energy of the crystal is found to be expressible as an integral having a well known form involving Einstein's expression for the average thermal energy of a harmonic oscillator.

It may be mentioned in conclusion that the method sketched above has been successfully applied to the evaluation of the specific heats of crystals—including especially diamond and the metallic elements—down to the very lowest temperatures approaching absolute zero. The theory emerges triumphantly from the test.

8. Summary

The fundamental notions of quantum theory and thermodynamics indicate that a crystal should be regarded as an assembly of an immense number of oscillators whose energy states are quantised and which form a system in thermodynamic equilibrium. They also indicate that the spectroscopic properties and the thermal behaviour of crystals stand in the closest relation to each other. We are thus left with the problem of discovering and enumerating the oscillators of the different sorts comprised in the crystal and of determining their scheme of energy levels. This may be done by methods analogous to those which have proved successful in the field of molecular spectroscopy. The results obtained are in perfect agreement with the observed spectroscopic properties and thermal behaviour of crystals.