

DEFECTS IN CRYSTAL LATTICES

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1. INTRODUCTION

A PERFECT crystal is one in which a regular arrangement of atoms extends periodically and indefinitely in space in all the three directions. It can be looked upon as a three-dimensional array of identical lattice cells within each of which the atoms are identically arranged. Such a crystal is only a concept and an idealisation and does not actually exist. However, the concept proved to be quite useful in understanding several properties of crystalline solids.

It was realised quite early that the theory of perfect crystals is not adequate to explain satisfactorily many interesting properties such as plastic deformation, ionic conductivity, diffusion, luminescence and some other mechanical, optical and electrical properties. It has been found necessary to postulate departures from perfection in the structures of crystals to explain such properties. Several kinds of imperfections or defects have thus come to be recognised and introduced from time to time. It has even been stated that the more interesting properties of crystalline solids depend on the defects in its assumed ideal structure rather than on the structure itself.

By an imperfection or a defect is meant any deviation from the perfect periodic order that should exist in an ideal crystal. The possible imperfections are usually classified as zero, one, two, and three-dimensional imperfections. If the deviations are localised and confined to the vicinity of a few atoms, they are zero-dimensional or point defects. If they extend along lines, they become one-dimensional or line defects. Two-dimensional or surface imperfections and three-dimensional or volume imperfections are conceived of and understood in a similar way. We shall be concerned with point defects only in this short survey.

2. POINT DEFECTS

It has been shown from considerations of entropy that even in a perfect crystal, there would exist in equilibrium a certain number of point imperfections at a given temperature. There are many kinds of point defects. The simplest one is a missing atom or a vacancy. In ionic crystals, there should be present as many vacancies of the positive ion as there are of the negative ion to ensure neutrality of the

crystal as a whole. Such vacancies are called *Schottky defects*.

Another kind of point defect appears when an atom or ion is displaced from its position into an interstitial position creating a nearby vacancy. Such a displacement occurs readily in structures which contain relatively large inter-atomic voids. Interstitial ions or atoms and consequent ion or atom vacancies are called *Frenkel defects*.

Presence of foreign atoms or ions either in the interstitial positions of the host structure or in the positions of the host atoms themselves by substitution are also regarded as point defects. These are called *interstitial and substitutional impurities* respectively.

It is not difficult to see that the density of a crystal may be expected to increase, remain unchanged, or decrease respectively with increasing defect concentration according as the defects are of the interstitial, Frenkel or Schottky type. Interstitials and vacancies, when present in considerable density, may interact to form clusters and give rise to interesting physical properties. Breckenridge¹ has pointed out that Schottky defects forming into pairs of opposite signs possess a dipole moment and should cause dielectric relaxation effects. Positive ion vacancies which are characterised by a negative charge get attached to divalent substitutional impurity ions in alkali halides and have been found to give rise to dielectric relaxation effects. In fact, various types of relaxation effects caused by point defects in crystals constitute an interesting group of physical properties and these have been the subject-matter of several recent studies.

3. RELAXATION PHENOMENA

It has just been pointed out that Schottky defect pairs and vacancies bound to divalent impurity ions can cause dielectric relaxation effects. One may expect that, under certain circumstances, they should cause the analogous mechanical effect as well, namely internal friction. The mechanical effect, when observed, has been explained as due to the non-equivalence of lattice points brought about by the strain in the lattice due to external stress. A special feature of the mechanical effects, as distinct from the electrical ones, is that they may be caused by uncharged point defects as well.

Calcium oxide (CaO) goes into solid solution in thorium oxide (ThO_2). The latter crystallises in the cubic system having the fluorite structure. In this structure, every thorium atom is at the centre of a cube and is surrounded by eight oxygen atoms situated at the corners of the cube. Each thorium atom replaced by a calcium has to result in an oxygen vacancy. This case is a good example of an ion vacancy of oxygen bound to a divalent impurity ion, namely calcium. For simplicity, the vacancy may be assumed to be confined to the first neighbour equivalent sites which are the corners of a cube. When there is no external field—mechanical or electrical—the vacancy will be jumping from one site to another in the first neighbour sites and has an equal occupation probability in respect of each one of them. When an external field is imposed, this equality of probability will be disturbed and a small deviation therefrom will set in. On removal of the field, the disturbed probability distribution decays into the equilibrium distribution. Hoffman² has pointed out that this decay for a finite system can in general be described with the help of a finite number of normal relaxation modes. A relaxation mode is a probability distribution for the vacancy which decays on all sites with the same characteristic decay or relaxation time. We may recall here that a general displacement mode for a finite set of particles bound to each other as a dynamical system can be described with the help of a finite number of normal vibrational modes. Haven³ pointed out that there is a close analogy between the relaxation modes of a set of sites and vibrational modes of a molecule. The relaxation times correspond to normal frequencies and deviation of probabilities of occupation from equilibrium distribution corresponds to deviation of the atomic positions from the equilibrium ones. Just as the symmetry of atomic positions enable the application of group theory to a study of the normal modes of vibration, the symmetry of the system of sites accessible to the vacancy enables the application of group theory for classifying the relaxation modes.

The relaxation modes as well as the components of the external field can be classified as possessing the symmetry of one or other of the irreducible representations of the point group of the system of sites under consideration. It follows that a particular external field can cause relaxation, if only there is a mode which has the same symmetry. The subject has recently been deve-

loped in some detail by Wachtman⁴ and by Bhagavantam and Pantulu.⁵ When the point defect is free to move on all the equivalent sites throughout the crystal, it is called a free defect. The mechanical relaxation effects caused by such defects can be studied by extending the methods applied to bound or trapped point defects in the same way in which studies on the normal vibrations of molecules have been extended to study such vibrations in crystals.

4. EXAMPLE OF ThO_2 - CaO SYSTEM

It has been mentioned that ThO_2 - CaO system is a good example and that each thorium atom replaced by a calcium results in an oxygen vacancy. Among others, this system has recently been studied by Wachtman. If the oxygen vacancy is assumed to be trapped to the calcium located at the centre of a cube, the eight nearest neighbour oxygen sites, which the vacancy can occupy with equal probability in the absence of an external field, have the symmetry of the O_h group. The symmetry types of the irreducible representations in respect of this group, the representations under which the relaxation modes are possible and the manner in which the components of an external electric or mechanical field tensor can be classified have been given by Bhagavantam and Pantulu. One relaxation mode coming under F_{2u} which is a triply degenerate representation is found to be electrically active. Another mode coming under F_{2g} which is also a triply degenerate representation is mechanically active. There is a mode coming under A_{1u} which is neither mechanically active nor electrically active. The types F_{2u} and A_{1u} are antisymmetric and the type F_{2g} is symmetric with respect to the centre of inversion. These conclusions are similar to the results relating to normal modes of vibration in respect of a molecule with O_h symmetry, namely, that those coming under F_{2u} are active in infra-red absorption, those coming under F_{2g} are active in Raman scattering and those coming under A_{1u} are inactive in both infra-red absorption and Raman scattering. These conclusions have been reached by Wachtman and also by Bhagavantam and Pantulu. One can obtain the relaxation times as well in respect of these modes. The mode F_{2g} is estimated to have a relaxation time which is just twice that of the mode F_{2u} . That this is in fact so in calcium doped thorium oxide has been verified experimentally by Wachtman and his collaborators.

There are many other cases of significant practical importance which can be brought within the purview of such studies, but those are not discussed here. As has already been pointed out in the literature, there is a need for studying experimentally both the electrical and mechanical relaxation effects on the same samples of crystals. The close analogy that exists between the normal vibrations on the one hand and relaxation modes on the other also enables group theoretical methods which have already been successfully applied in the former case being extended to the latter as well. There is scope for extending such studies to investigate

the influence which defects in crystal lattices are likely to exert on a variety of physical properties particularly in relation to crystal symmetry.

1. Breckenridge, *Imperfections in Nearly Perfect Crystals*, Ed. W. Shockley, John Wiley & Sons, 1952.
2. Hoffman and Pfeiffer, *J. Chem. Phys.*, 1954, **22**, 132.
3. Haven and Van Santer, *Nuovo Cimento, Supple-mento VII*, 1957, p. 605.
4. Wachtman, Jr., *Physical Review*, 1963, **131**, 517.
5. Bhagavantam and Pantulu, *Proc. Ind. Acad. Sci.*, 1963, **58**, 183.

MOLECULAR HYDROGEN IN INTERSTELLAR SPACE

EXTENSIVE radio observations of our galaxy have shown that there are vast regions containing neutral atomic hydrogen at an average density of 1 atom/cm.³ Also the 21-cm. scanning of interstellar space has given strong evidence that the hydrogen is distributed in dense "clouds" in which the density is about as much as 10 atoms/cm.³, and that these H I clouds fill roughly 10% of the interstellar space, their average kinetic temperature being about 100° K.

At this temperature hydrogen gas even at the low density of 10 atoms per cm.³ would be almost completely molecular if thermal equilibrium existed. However, the conditions in H I clouds are very far from thermal equilibrium, and a gas initially purely atomic will be converted very slowly into molecular form.

In two theoretical papers contributed to the *Astrophysical Journal*, R. J. Gould, E. E. Salpeter and T. Gold discuss the various plausible processes whereby molecular hydrogen may be formed in interstellar space. The most efficient mechanism for the formation of H₂ is the catalytic process of recombination reaction on the surface of the interstellar grains, first suggested by van de Hulst. Interstellar grains appear to have physical properties that make them efficient catalysts for the formation of molecular hydrogen. Gould and Salpeter show that this process of association on the surface of the interstellar grains has a characteristic time possibly as short as 10⁸ years, which is two orders of magnitude less than the age of the galaxy. Thus known physi-

cal processes can produce a high abundance of molecular hydrogen. However, at present, there is no easy way of detecting interstellar molecular hydrogen. Spectroscopic detection of interstellar H₂ is extremely difficult. The first bound excited electronic state of the molecule (11 ev.) gives absorption in the inaccessible ultra-violet. Being homopolar, the molecule has no permanent dipole moment, so that its pure vibration-rotation absorption is very weak. Moreover, the molecule has no fine or hyperfine structure splitting in the ground state, so that there can be no detection by radio emission analogous to that of the 21-cm. line of atomic hydrogen. Experiments in this direction, however, are underway which may prove successful. For example, The Princeton Observatory's spectroscopy-carrying satellite to detect ultra-violet absorption lines; observation of near infra-red vibration-rotation radiation from H₂ near hot stars as suggested by Gould and Harwit.

If there is a high abundance of H₂ as is predicted by the present calculations of the authors, and also as has been suspected for nearly two decades, the H I clouds temperature is likely to be closer to 50° K.—since hydrogen molecule is an effective cooling agent—than to 100° K. as initially given by the 21-cm. investigators. In this connection it may be emphasized that the latest 21-cm. investigations by Radhakrishnan et al. actually do point to a lower temperature, and this may be taken as weak evidence for a high molecular abundance.—(*Astrophys. J.*, 1963, **138**, 391.)