

# POINT DEFECTS AND RELAXATION PHENOMENA IN CRYSTALS

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## 1. INTRODUCTION

LATTICE imperfections are known to cause relaxation effects in the electrical and mechanical properties of crystals. In fact, a study of dielectric losses and of internal friction provides a method for studying lattice defects in crystals. In this paper, we shall confine ourselves to a study of two kinds of point defects.

The first kind are called 'trapped point defects' and are defects which can occupy any one of a limited set of equivalent positions in the neighbourhood of a trapping centre. Cation vacancies in alkali halides, when each one of such vacancies is captured by a divalent impurity cation, are examples of this kind. A specific case is that of NaCl containing a small amount of calcium. A certain number of  $\text{Ca}^{++}$  ions will occupy  $\text{Na}^+$  positions in the crystal and each  $\text{Ca}^{++}$  ion will be associated with a  $\text{Na}^+$  vacancy, thus compensating for the excess charge. Under equilibrium conditions, the vacancy is assumed to move into any one of the twelve first neighbour  $\text{Na}^+$  sites with the same probability, as it is bound by electrical forces to the  $\text{Ca}^{++}$  ion (Haven and Van Santen, 1957).

The second kind are called 'free point defects'. Such defects can occupy all equivalent positions throughout the crystal by jumping from one site to another in the structure. A specific case is that of rutile ( $\text{TiO}_2$ ) which has a simple tetragonal lattice. It can be made to lose oxygen by heating in reduced oxygen pressure. It is assumed that such a loss results in the formation of oxygen vacancies in the structure. There are four oxygen sites per lattice point and an oxygen vacancy can occupy not only any one of these four sites but also wander into all other equivalent positions in the structure and occupy them with equal probability under equilibrium conditions (Wachtman, 1962).

We propose to study the relaxation phenomena arising from both the types of point defects cited above, employing group theoretical methods

and laying special emphasis on an analogy that runs between the theory of normal oscillations in molecules and crystals on the one hand and the theory of relaxation phenomena in cases of trapped and free point defects on the other.

A certain amount of work has recently been published by Haven and Van Santen (1954, 1957) and by Wachtman and his associates (1962, 1963) on these lines and most of the results obtained by them also come out of the unified theory that we are now presenting and are confirmed by us. Reference is made to such instances at appropriate places in the paper. One merit of the theory now developed and the analogy referred to above is that they enable us to utilise a large volume of results already available in published literature in regard to normal oscillations of molecules and crystals and study the relaxation effects in several new instances.

## 2. TRAPPED POINT DEFECTS

A trapped point defect may, in the first approximation, be assumed to be confined to the nearest neighbouring sites around a trapping centre. These will, of course, be of one kind so that they are all accessible to the point defect with the same probability in the absence of an external field. When a field like an electric field or a stress is applied, the probability distribution of the system deviates from the equilibrium distribution. On removal of the field, the deviated distribution will decay until equilibrium is reached. Let us consider a finite system of  $n$  sites and endow each site with a single degree of freedom, namely a small deviation from the equilibrium probability with which it is accessible to a point defect.

The analogy with the theory of small oscillations of a finite number of mass particles is at once apparent. It may be noted that whereas in the case of small oscillations, the number of degrees of freedom associated with  $n$  mass particles is  $3n$ , in this case the number of degrees of freedom associated with  $n$  sites is  $n$  only. It can be shown (Hoffman, 1954; Wachtman, 1963) that the behaviour of the system is governed by  $n$  simultaneous first-order linear differential equations for the occupation probabilities of the point defect on the  $n$  sites. There are  $n$  independent solutions corresponding to  $n$  eigen values characteristic of the system. Any general solution which represents a general decay is a linear combination of the  $n$  independent solutions.

The eigen vectors corresponding to the eigen values are called the relaxation modes and these correspond to the normal modes in the theory of small

oscillations. The eigen values are related to the relaxation times of the system. The spectrum of relaxation times corresponds to the spectrum of normal frequencies. A particular relaxation mode is an expression of the probability distribution in that mode in regard to the  $n$  sites and the distribution decays with the same relaxation time at all the sites. This corresponds to the fact that in a normal mode of oscillation, every oscillating atom has the same periodic time and hence the same frequency. It is immediately evident that group theory can be applied with the same advantage to a study of the relaxation phenomena due to point defects as it was done to a study of molecular dynamics.

The sites accessible to a point defect will have the symmetry of the appropriate point group. A matrix representation of the point group consisting of permutation matrices is formed and this is called the 'immediate representation' (Wachtman, 1963). The permutation matrices are found in the following way. The sites are numbered in a particular order. The effect of a symmetry operation is to take some sites into others which effect can be represented by a permutation on the order numbers of the sites. Thus for every symmetry operation, there is a permutation and from the group of symmetry operations we generate a group of permutations. Further, every permutation may be regarded as being caused by a matrix operator operating on the order number of the sites. Thus for every permutation there is a matrix and we obtain a matrix representation.

The immediate representation  $\Gamma(\mathbf{I})$  of the point group under consideration can be reduced to a direct sum of irreducible representations in a unique way. This fact can be symbolically written as

$$\Gamma(\mathbf{I}) = \sum_i a_i \Gamma^i$$

where  $a_i$  is the number of times  $\Gamma^i$  occurs in  $\Gamma(\mathbf{I})$ . Let  $\chi(\mathbf{R})$  be the character of a group element  $\mathbf{R}$  in  $\Gamma(\mathbf{I})$  and  $\chi_i(\mathbf{R})$  be its character in  $\Gamma^i$ . Then  $a_i$  is given by

$$a_i = \frac{1}{N} \sum_{\rho} h_{\rho} \chi_{\rho}^i(\mathbf{R}) \chi(\mathbf{R}) \quad (1)$$

where  $\rho$  refers to the class to which  $\mathbf{R}$  belongs and  $h_{\rho}$  is the number of elements in the class.  $N$  is the order of the group. The character  $\chi(\mathbf{R})$  is the number of sites that remain invariant on an application of the operation  $\mathbf{R}$ .

The eigen vectors, which we referred to as relaxation modes, form the basis of these irreducible representations. This is equivalent to stating that

the linear manifold of eigen vectors formed by the entire set of relaxation modes splits into sets of sub-manifolds each forming a basis for an irreducible representation.

An understanding of the problem requires the determination of (i) the relaxation modes, (ii) the relaxation times, (iii) the selection rules governing the activity of various modes: electrical, mechanical or otherwise; and (iv) the components of the external field that can excite a particular mode.

The relaxation times are negative reciprocals of the roots of the characteristic equation. Under the assumption that all sites are equivalent, which means that the jump probability between any two neighbouring sites is the same, the characteristic determinants usually have simple forms enabling a direct evaluation of the roots. Even otherwise, the relaxation modes which are the eigen vectors of the characteristic equation and possess specific types of symmetry can often be found by inspection. The relaxation modes thus obtained will enable us to find the eigen values by diagonalising the characteristic matrix. An alternative way would be to compute the rate of decay at a particular site and obtain therefrom the relaxation time for a particular mode. This method is illustrated in greater detail by giving a simple rule and applying the same to specific cases in Section 3.

To determine which modes are electrically or mechanically active, the following procedure is adopted. Strain is a second rank symmetric tensor, and the transformation matrices of the components of the strain tensor corresponding to the symmetry operations of the group form a sixth order representation  $\Gamma(S)$  of the group. The characters of the group elements in this representation are given by

$$\chi_s(\mathbf{R}) = 2 \cos \phi (\pm 1 + 2 \cos \phi) \quad (2)$$

$\chi_s(\mathbf{R})$  is the character of the group element  $\mathbf{R}$ , the suffix  $s$  referring to the representation induced by the symmetric tensor. Where the alternative sign occurs,  $+$  is to be taken when  $\mathbf{R}$  is a pure rotation through  $\phi$  and  $-$  is to be taken when  $\mathbf{R}$  is a rotation through  $\phi$  followed by a reflection in a plane perpendicular to the axis of rotation. The representation can be reduced in the same manner as the immediate representation using  $\chi_s(\mathbf{R})$  in place of  $\chi(\mathbf{R})$  in formula (1). The result is written symbolically as

$$\Gamma(S) = \sum_i b_i \Gamma^i.$$

The selection rule for mechanical activity is the following. Irreducible representations which occur simultaneously in  $\Gamma(\mathbf{I})$  and  $\Gamma(S)$  have a special

significance in the context of our problem. All relaxation modes which possess the same symmetry pattern dictated by the characters appropriate to one or other of the simultaneously occurring irreducible representations will be mechanically active. To determine which components of the strain tensor are capable of exciting a particular mechanically active mode, we have to resolve the linear space formed by the tensor components into its irreducible sub-manifolds which form the basis vectors of the irreducible representations in  $\Gamma(S)$ . Such of the components of the strain tensor or linear combinations thereof which possess the same symmetry as that of the relaxation mode under consideration will excite the mode.

A similar rule for electrical activity can be given using the characters  $\chi_v(\mathbf{R})$  in the representation  $\Gamma(V)$  induced by the components of a vector in formula (1). Those modes coming under irreducible representations which occur in  $\Gamma(I)$  as well as in  $\Gamma(V)$  will be electrically active.

It is worthwhile pointing out that the above rules are exactly analogous to the selection rules governing the activity of a normal mode of oscillation in Raman effect and Infra-red absorption respectively. This analogy flows from the fact that Raman effect is the result of changing optical polarizability which is a symmetric tensor and Infra-red absorption is the result of changing electric moment which is a polar vector. The required analysis of the components of a symmetric tensor and of the components of a polar vector has already been carried out for several point groups and the results are readily available in standard treatises dealing with molecular spectra and Raman effect (Placzek, 1934; Herzberg, 1945). Examples worked in Section 3 illustrate the details of procedure. Although our procedure is general and applicable to any case, only such examples for which results from previous workers are available are included to enable comparison.

### 3. SPECIFIC EXAMPLES OF TRAPPED POINT DEFECTS

The ( $\text{Ca}^{++} - \text{Na}^+$  vacancy) system in NaCl, already mentioned in the introduction, will now be considered. Figure 1 shows the twelve  $\text{Na}^+$  sites numbered in a particular order. The  $\text{Ca}^{++}$  which is at the body centre of the cube is not shown.

The twelve sites constitute a point group with  $O_h$  symmetry. The characters of the  $O_h$  group are given in Table I.

The characters in the representation  $\Gamma(I)$  are shown against row  $\chi(\mathbf{R})$ . Applying equation (1), the structures of  $\Gamma(I)$ ,  $\Gamma(V)$  and  $\Gamma(S)$  are determined and given in the character table under columns  $\Gamma(I)$ ,  $\Gamma(V)$  and  $\Gamma(S)$  respectively. The irreducible representations are denoted by the symmetry

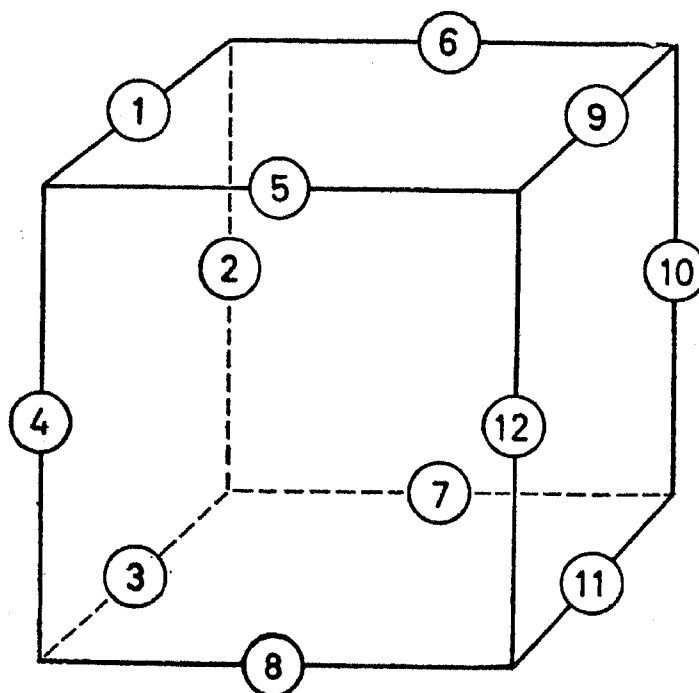


FIG. 1

TABLE I

Characters of the  $O_h$  group

$O_h$	E	$8C_3$	$3C_2$	$6\sigma$	$8S_6$	$i$	$3S_4$	$3\sigma$	$6C_2$	$6C_4$	$\Gamma(\Gamma)$		$\Gamma(V)$	$\Gamma(S)$	V	S
											NaCl	ThO <sub>2</sub>				
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	1	1	0	1	..	$(xx+yy+zz)$
$A_{2g}$	1	1	1	-1	-1	1	1	1	-1	-1	0	0	0	0	..	..
$E_g$	2	-1	2	0	0	2	-1	2	0	0	1	0	0	1	..	$(xx+yy-2zz)$ $(xx-yy)$
$F_{1g}$	3	0	-1	-1	1	3	0	-1	-1	1	0	0	0	0	..	..
$F_{2g}$	3	0	-1	1	-1	3	0	-1	1	-1	1	1	0	1	..	$(xy, yz, zx)$
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1	0	1	0	0	..	..
$A_{2u}$	1	1	1	-1	-1	-1	-1	-1	1	1	0	0	0	0	..	..
$E_u$	2	-1	2	0	0	-2	1	-2	0	0	0	0	0	0	..	..
$F_{1u}$	3	0	-1	-1	1	-3	0	1	1	-1	1	0	0	0	..	..
$F_{2u}$	3	0	-1	1	-1	-3	0	1	-1	1	1	1	1	0	$(x, y, z)$	..
$\chi(R)$																
NaCl	12	0	0	2	0	0	0	4	2	0						
ThO <sub>2</sub>	8	2	0	4	0	0	0	0	0	0						

species notation commonly used in molecular vibrations (Bhagavantam and Venkatarayudu, 1962). The column under S gives the irreducible sub-manifolds of the symmetric tensor components appropriate to the  $O_h$  symmetry. The column under V gives a similar result for the vector components. The interpretation of the table is straightforward. The symmetry species (irreducible representations)  $E_g$  and  $F_{2g}$  are mechanically active. They can be excited respectively by the strain components  $xx, yy, zz$  and  $xy, yz, zx$ . Similarly  $F_{2u}$  is electrically active and can be excited by the components  $x, y$  or  $z$  of the electric vector. The symmetry species  $F_{1u}$  is neither electrically nor mechanically active. Analogous to this is the result that in molecular dynamics, we do get normal modes which are neither active in Raman effect nor in infra-red absorption.

The relaxation modes are given below.

$A_{1g}$	( 1	1	1	1	1	1	1	1	1	1	1	1)
$E_g$	(-2	1	-2	1	1	1	1	1	-2	1	-2	1)
	( 0	1	0	1	-1	-1	-1	-1	0	1	0	1)
$F_{2g}$	( 1	0	-1	0	0	0	0	0	-1	0	1	0)
	( 0	0	0	0	-1	1	-1	1	0	0	0	0)
	( 0	1	0	-1	0	0	0	0	0	-1	0	1)
$F_{1u}$	( 1	0	-1	0	-1	-1	1	1	1	0	-1	0)
	( 0	-1	0	1	-1	1	1	-1	0	-1	0	1)
	(-1	1	-1	1	0	0	0	0	1	-1	1	-1)
$F_{2u}$	(-1	-1	-1	-1	0	0	0	0	1	1	1	1)
	( 0	1	0	-1	-1	1	1	-1	0	1	0	-1)
	( 1	0	-1	0	1	1	-1	-1	1	0	-1	0)

The eigen vectors given above under each one of the symmetry species have not been normalized. The twelve numbers in each vector represent the components of the vector and refer to the twelve sites in the order shown in Fig. 1. They are proportional to the deviations of the occupation probability from the equilibrium value.

As has already been mentioned, the relaxation times are usually computed by solving the characteristic equation. Assuming that the  $Na^+$  vacancy jumps from any site to a neighbouring site with a jump probability  $k$  in the equilibrium state, the relaxation time  $\tau$  obtained for each of the modes is given below. The results agree with Haven's values (1957) for this case.

Symmetry Species	$A_{1g}$	$E_g$	$F_{2g}$	$F_{1u}$	$F_{2u}$
$\tau$	$\infty$	$\frac{1}{6k}$	$\frac{1}{4k}$	$\frac{1}{6k}$	$\frac{1}{2k}$

A simple rule to find the relaxation time has been formulated by us and given in (3). This rule is obtained by evaluating the rate of decay at any site due to jumps occurring from this site to its neighbours or *vice versa* in a given relaxation mode.

$$\tau = \frac{p_i}{k \sum_j (p_i - p_j)} \quad (3)$$

In (3),  $p_i$  is the probability index associated with the  $i$ -th site in a particular mode, at which we wish to evaluate the decay.  $p_j$  is the corresponding index for the neighbouring site  $j$ .  $k$  has the same significance as before. The summation extends over all the nearest neighbours of  $i$ . By applying this rule, one may verify not only the results given above in respect of the relaxation times for the different modes of the  $O_h$  group but also the results given

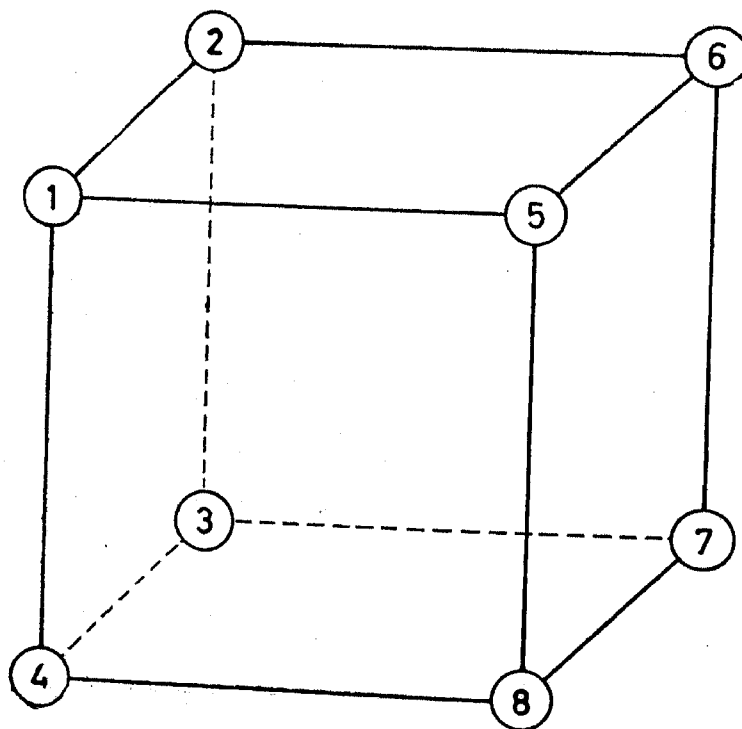


FIG. 2



in the literature (Haven, 1954; Hoffman, 1954) or obtain the relaxation times for the modes in any other case.

Thorium oxide (Fluorite structure) with calcium impurity will now be considered as a second example of trapped point defects. The oxygen vacancy is trapped to a calcium centre and can occupy the eight nearest neighbouring oxygen sites with equal probability in the absence of an external field. The sites are at the corners of a cube and have the symmetry of the  $O_h$  group. They are numbered in the order shown in Fig. 2.

Following the procedure outlined above, the structure of the representation  $\Gamma(I)$  is determined and shown in Table I under column  $\Gamma(I)$ . A comparison with columns  $\Gamma(V)$  and  $\Gamma(S)$  shows that  $F_{2u}$  is electrically active and  $F_{2g}$  is mechanically active.  $A_{1u}$  is neither electrically nor mechanically active.  $F_{2g}$  may be excited by strain components  $xy$ ,  $yz$ ,  $zx$  as shown by column S. These conclusions are in agreement with those derived by Wachtman (1963).

The relaxation modes for  $\text{ThO}_2$ -Ca system are given below.

$A_{1g}$	( 1 1 1 1 1 1 1 1 )
$A_{1u}$	( 1 -1 1 -1 -1 1 -1 1 )
$F_{2g}$	( 1 -1 -1 1 -1 1 1 -1 ) ( 1 1 -1 -1 -1 -1 1 1 ) ( -1 1 -1 1 -1 1 -1 1 )
$F_{2u}$	( 1 1 1 1 -1 -1 -1 -1 ) ( 1 -1 -1 1 1 -1 -1 1 ) ( 1 1 -1 -1 1 1 -1 -1 )

The relaxation times obtained for the above normal modes from the general rule (3) are as follows:

Symmetry Species	$A_{1g}$	$A_{1u}$	$F_{2g}$	$F_{2u}$
$\tau$	$\infty$	$\frac{1}{6k}$	$\frac{1}{4k}$	$\frac{1}{2k}$

Any other point defect in any crystal which can occupy a set of sites with  $O_h$  symmetry can be dealt with using Table I. We have only to determine

$\Gamma(I)$  for the system of sites and carry the analysis through in the manner explained above.

#### 4. FREE POINT DEFECTS

The free point defects can wander at random and occupy equivalent sites throughout the crystal. Such defects can therefore contribute to electrical conductivity if they are electrically charged defects. In this paper, however, we shall confine ourselves to the mechanical effects.

If there is an external stress, a strain will be induced in the crystal and following Wachtman (1963), we may assume that the strain will introduce an inequivalence resulting in the system having different energies when the point defect is placed in two inequivalent sites. This causes relaxation effects leading to internal friction.

The theory given for the trapped defects can easily be extended to the case of free point defects. The relationship between the theory in regard to trapped defects and the theory in regard to freely moving point defects is analogous to the relationship that exists between oscillations of molecules or groups of finite number of atoms on the one hand and of crystals built from such units by repetition in space on the other (Bhagavantam and Venkatarayudu, 1962). It is assumed that the strain is homogeneous throughout the crystal. This preserves the equivalence of unit cells even when the crystal is under strain. It is then reasonable to assume that what happens in one unit cell happens in all the equivalent cells. Under this assumption, we may confine ourselves to the study of one unit cell. This simplification is effected by regarding all translations in the group of symmetry operations of the crystal as equivalent to identity. The factor group thus formed is isomorphic with one of the thirty-two crystallographic point groups. The considerations derived for trapped defects are then applied to the set of equivalent sites associated with a lattice point. We shall illustrate the method by considering one example. The example has been so chosen that our result can be compared with those of Wachtman and his associates (1963).

#### 5. AN EXAMPLE OF FREE POINT DEFECTS

Rutile ( $\text{TiO}_2$ ) belongs to the tetragonal system, has a simple lattice and the space group  $D_{4h}^{14}$ . There are two titanium atoms and four oxygen atoms per lattice point. We can conceive of three kinds of point defects for this structure (Wachtman, 1963), namely (i) titanium vacancies, (ii) oxygen vacancies, and (iii) titanium interstitials. In Fig. 3, the titanium positions, confining ourselves to only those associated with the smallest Bravais cell

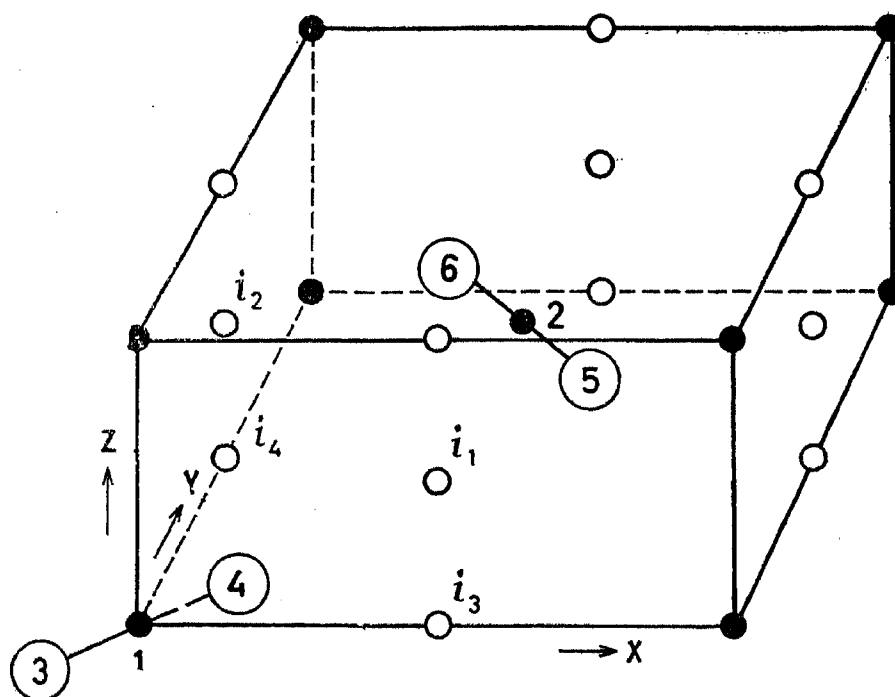


FIG. 3

or a single lattice point, are numbered 1 and 2. All other titanium positions have not been numbered as they are equivalent to either 1 or 2. The oxygen positions, similarly chosen, are numbered 3, 4, 5 and 6. Titanium interstitials, if they are present, can occupy positions at the centres of the four rectangular faces and at the centres of eight equal sides of the tetragon. They are shown as small hollow circles in the figure and the four interstitial sites associated with a single lattice point are numbered  $i_1$ ,  $i_2$ ,  $i_3$  and  $i_4$ .

Now we need consider only the number of sites in the smallest Bravais cell and conduct the analysis as before, making use of the point group  $D_{4h}$  which is isomorphic with the factor group mentioned. The group of symmetry operations and the corresponding permutation group for the case under consideration are given below. Permutations of interstitial positions under each symmetry operation are not given. They may be easily worked out.

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E	..	(1)	(2)	(3)	(4)	(5)	(6)
$2C_4'$	..	(1 2)	(3 6 4 5)				
		(1 2)	(3 5 4 6)				
$C_2$	..	(1)	(2)	(3 4)	(5 6)		

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$2C_2'$	..	(1 2)	(3 5)	(4 6)	
		(1 2)	(3 6)	(4 5)	
$2C_2''$	..	(1)	(2)	(3)	(4) (5 6)
		(1)	(2)	(3 4)	(5) (6)
$i$	..	(1)	(2)	(3 4)	(5 6)
$2S_4$	..	(1 2)	(3 5 4 6)		
		(1 2)	(3 6 4 5)		
$\sigma_h$	..	(1)	(2)	(3)	(4) (5) (6)
$2\sigma_v'$	..	(1 2)	(3 6)	(4 5)	
		(1 2)	(3 5)	(4 6)	
$2\sigma_v''$	..	(1)	(2)	(3 4)	(5) (6)
		(1)	(2)	(3)	(4) (5 6)

The characters of  $D_{4h}$  are given in Table II.

TABLE II  
Characters of the  $D_{4h}$  group

$D_{4h}$	E	$2C_4'$	$C_2$	$2C_2'$	$2C_2''$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v'$	$2\sigma_v''$	$\Gamma(I)$			$\Gamma(S)$	S
											Ti	O	Ti (int.)		
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	1	1	1	2	$(xx+yy); (xz)$
$A_{2g}$	1	1	1	-1	-1	1	1	1	-1	-1	0	0	1	0	..
$B_{1g}$	1	-1	1	1	-1	1	-1	1	1	-1	0	0	1	1	$(xx-yy)$
$B_{2g}$	1	-1	1	-1	1	1	-1	1	-1	1	1	1	1	1	$(xy)$
$E_g$	2	0	-2	0	0	2	0	-2	0	0	0	0	0	1	$(yz, zx)$
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1	0	0	0	0	..
$A_{2u}$	1	1	1	-1	-1	-1	-1	-1	1	1	0	0	0	0	..
$B_{1u}$	1	-1	1	1	-1	-1	1	-1	-1	1	0	0	0	0	..
$B_{2u}$	1	-1	1	1	1	-1	1	-1	1	-1	0	0	0	0	..
$E_u$	2	0	-2	0	0	-2	0	2	0	0	0	1	0	0	..
$\Pi$	2	0	2	0	2	2	0	2	0	2					
$\chi(R)O$	4	0	0	0	2	0	0	4	0	2					
Ti(int.)	4	0	4	0	0	4	0	4	0	0					

The compound characters  $\chi(R)$  in the immediate representations  $\Gamma(I)$  appropriate to the three kinds of free defects mentioned are shown in the three rows Ti, O, and Ti (int.). The structures of the representations  $\Gamma(I)$  are determined using formula (1) and given under columns Ti, O, Ti (int.). The column under  $\Gamma(S)$  refers as before to the representation induced by a symmetric tensor and column S to the resolution of the components of the symmetric tensor into sub-manifolds with symmetry appropriate to the irreducible representations into which they fall. From a comparison of columns under  $\Gamma(I)$ ,  $\Gamma(S)$  and S, we conclude that titanium vacancies can cause internal friction under strain  $xy$  only. Similarly, oxygen vacancies can cause internal friction under strain  $xy$  only. Titanium interstitials can cause internal friction under strains  $xx$ ,  $yy$  or  $xy$  only.

We can now consider the group of titanium interstitials  $i_1, i_2, i_3$  and  $i_4$  associated with a single lattice point. The relaxation modes coming under the appropriate symmetry species are given below.

$$\begin{array}{ll} A_{1g} & (1 \quad 1 \quad 1 \quad 1) \\ A_{2g} & (1 \quad -1 \quad 1 \quad -1) \\ B_{1g} & (1 \quad -1 \quad -1 \quad 1) \\ B_{2g} & (1 \quad 1 \quad -1 \quad -1) \end{array}$$

If we make the assumptions that a titanium can get into all the four interstitial positions with the same probability without reference to geometrical distances between them and that the probability of a jump taking place into or from, say a site  $i_1$  to  $i_2, i_3$  and  $i_4$  is the same, it follows that rule (3) already derived can be used for obtaining the relaxation time appropriate to any mode. It may be noted that the analysis also presumes that what is true of a set of interstitials associated with a lattice point is always true of sets associated with all other lattice points in the crystal. In this case, the result comes out as  $\tau = 1/4k$  for  $A_{2g}, B_{1g}$  and  $B_{2g}$ .

During the course of this work, the authors had the benefit of correspondence and of receiving some preprints of his work from Mr. J. B. Wachtman, Jr., of the National Bureau of Standards and would like to express their thanks for the same.

## 6. SUMMARY

Group theoretical methods are developed for studying two types of point defects in crystals, namely trapped and untrapped ones, and the relaxation phenomena that arise therefrom. It is pointed out that a very close

analogy exists between the relaxation modes on the one hand and normal oscillations on the other. This analogy enables us to utilise many of the concepts developed and the results obtained earlier in connection with studies on molecular spectra and Raman effect for an investigation of the relaxation phenomena. Simple rules are given for writing out the modes, ascertaining their activity or otherwise in regard to external electric and mechanical fields, evaluating the relaxation times and so on. Specific examples which are of practical interest are worked out under both the classes of defects studied. The methods developed can be applied to any general case.

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