

TRAPPED POINT DEFECTS IN CRYSTALS: SIMULTANEOUS OCCURRENCE OF TWO VACANCIES

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ABSTRACT

Group theoretical methods have been used for obtaining the relaxation modes and relaxation times for the case of two vacancies simultaneously occurring when a crystal with CsCl structure has a trivalent impurity like Pr^{3+} introduced substitutionally.

1. INTRODUCTION

THE study of dielectric and mechanical relaxation due to point defects in crystals has attracted considerable attention in recent times.¹⁻⁴ Vacancies trapped in the vicinity of impurity ions in ionic crystals are one kind of point defects. A point defect of this kind can occupy any one of the crystallographically equivalent sites in the neighbourhood of the impurity by moving from one site to another. The dielectric and mechanical effects of such dipolar complexes are satisfactorily described by introducing the concepts of relaxation modes and relaxation times. These concepts are analogous to those related to normal modes and normal frequencies in the problem of small oscillations. It has been shown¹ that group theoretical methods developed for the study of small oscillations of symmetrical molecules can be adapted with advantage to determine the relaxation modes and times.

All cases so far studied consist of systems in which each impurity ion is associated with a single vacancy. On the other hand, in the case of a trivalent ion like Praseodymium (Pr^{3+}) substitutionally introduced into CsCl or KCl, we may expect two Cs^+ or K^+ ion vacancies associated with each impurity ion. The problem of determining the relaxation modes and times for such a system is studied in the present paper.

2. METHOD

To a first approximation we can assume that the vacancies lie entirely in the first neighbour (f.n.) sites. CsCl has a B.C.C. structure and the

6 f.n. atoms are octahedrally situated. A pair of these 6 sites is simultaneously occupied by the vacancies and there are 6C_2 ways of doing this. We label the sites by numbers 1, 2, 3, 4, 5, 6 and label the fifteen possible pairs by (12), (13), (14), (15), (16), (23), (24), (25), (26), (34), (35), (36), (45), (46), (56). The symmetry group of the sites is O_h . The probability of finding a vacancy pair in the site pair ($\alpha\beta$) may be denoted by $p_{\alpha\beta}$. In the equilibrium state $p_{\alpha\beta} = 1/15$ for all ($\alpha\beta$).

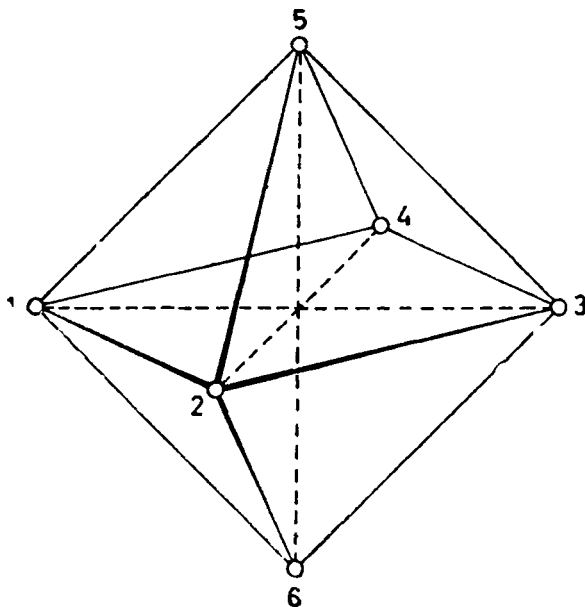


FIG. 1

We assume that a vacancy can jump only to one of the four near neighbours in the octahedron (Fig. 1). We will have to distinguish between some of the configurations of the two vacancies. For example, the probability of the vacancies occupying oppositely oriented sites is more than their occupying neighbouring sites. This fact necessitates the use of more than one jump frequency. If the vacancies are initially at neighbouring sites, say (12), the pair can change in six different ways. A jump of (12)-(15), accomplished by a jump of 2-5, is made with a frequency K . A return jump from (15)-(12) is also made with a frequency K . A change of (12)-(13) which involves a jump 2-3 for a vacancy, is from a less probable state to a more probable state and we postulate a frequency Ka for such a jump. The return jump (13)-(12) is made with frequency K/a . a is an arbitrary constant. We neglect simultaneous jumps like 1-4 and 2-3 which change (12)-(34).

Each symmetry operation of the crystal permutes the 15 pairs among themselves. The set of 15×15 matrices which perform the same permutation on the site pairs as the group operations themselves form a representation of the group called the Immediate Representation $\Gamma(\mathbf{I})$. The character $\chi(\mathbf{R})$ of a group operation \mathbf{R} in the representation $\Gamma(\mathbf{I})$ is simply equal to the number of pairs left invariant by \mathbf{R} . $\Gamma(\mathbf{I})$ is resolved into a direct sum of irreducible representations Γ^i of the group O_h as in (i).

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

In (i), a_i is the number of times Γ^i occurs in $\Gamma(\mathbf{I})$ and is given by (ii),

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

where $\chi_{\rho}^i(\mathbf{R})$ is the character of \mathbf{R} in Γ^i , N is the order of the group, h_{ρ} is the number of elements in the ρ -th class to which \mathbf{R} belongs.

3. RESULTS

Table I gives the characters of the point group O_h . The last row against $\chi(\mathbf{R})$ gives the characters of the symmetry operations in the immediate representation formed by the pair of sites. The column under $\Gamma(\mathbf{I})$ gives the number of times each irreducible representation occurs in the representation $\Gamma(\mathbf{I})$.

TABLE I

O_h	E	$8C_3$	$3C_2$	6σ	$6S_4$	i	$8S_6$	3σ	$6C_2$	$6C_4$	$\Gamma(\mathbf{I})$	$\Gamma(\mathbf{V})$	$\Gamma(\mathbf{S})$
A_{1g}	1	1	1	1	1	1	1	1	1	1	2	0	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	..	0	0
E_g	2	-1	2	0	0	2	-1	2	0	0	2	0	1
F_{1g}	3	0	-1	-1	1	3	0	-1	-1	1	..	0	0
F_{2g}	3	0	-1	1	-1	3	0	-1	1	-1	1	0	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	..	0	0
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	..	0	0
E_u	2	-1	2	0	0	-2	1	-2	0	0	..	0	0
F_{1u}	3	0	-1	-1	1	-3	0	1	1	-1	1	0	0
F_{2u}	3	0	-1	1	-1	-3	0	1	-1	1	1	1	0
$\chi(\mathbf{R})$	15	0	3	3	1	3	0	7	3	1			

The relaxation modes form the basis vectors of the irreducible representation in (i). Table II gives the symmetry modes of relaxation. The modes have not been normalised.

TABLE II

		(12)	(13)	(14)	(15)	(16)	(23)	(24)	(25)	(26)	(34)	(35)	(36)	(45)	(46)	(56)
A_{1g}	..	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_{1g}	..	$-\frac{1}{2}$	1	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	1	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	1
E_g	..	1	0	1	-2	-2	1	0	1	1	1	-2	-2	1	1	0
		1	0	1	0	0	1	0	-1	-1	1	0	0	-1	-1	0
E_g	..	0	-1	0	0	0	0	-1	0	0	0	0	0	0	0	2
		0	1	0	0	0	0	-1	0	0	0	0	0	0	0	0
F_{2g}	..	0	0	0	1	-1	0	0	0	0	0	-1	1	0	0	0
		0	0	0	0	0	0	0	-1	1	0	0	0	1	-1	0
F_{1u}	..	-1	0	1	0	0	1	0	0	0	-1	0	0	0	0	0
		1	0	1	-1	-1	-1	0	0	0	-1	1	1	0	0	0
F_{2u}	..	1	0	-1	0	0	1	0	-1	-1	-1	0	0	1	1	0
		0	0	0	1	-1	0	0	-1	1	0	1	-1	-1	1	0
F_{2u}	..	-1	0	-1	-1	-1	1	0	0	0	1	1	1	0	0	0
		-1	0	1	0	0	-1	0	-1	-1	1	0	0	1	1	0
		0	0	0	1	-1	0	0	1	-1	0	1	-1	1	-1	0

Once the relaxation modes are obtained, it is a straightforward matter to determine the relaxation times. We have, quoting from an earlier paper of Bhagavantam and Pantulu, the relaxation time τ_i corresponding to irreducible representation Γ^i given by

$$\tau_i = \frac{p_{\alpha\beta}}{\sum_{\gamma\delta} \omega_{\gamma\delta}^{\alpha\beta} p_{\alpha\beta} - \omega_{\alpha\beta}^{\gamma\delta} p_{\gamma\delta}}$$

where $(\gamma\delta) = (12), (13), \text{etc.}$ and $\omega_{\gamma\delta}^{\alpha\beta}$ is the jump frequency $(\alpha\beta) - (\gamma\delta)$. We may note that in selecting the site, say (12) in the expression for τ_i , all sites for which the p value is zero should be avoided because such a situation will lead to an indeterminate fraction. This results from the fact that if there is no finite deviation of probability at any given site from its equilibrium value, there is no relaxation occurring and therefore there

is no question of a relaxation time. It does not, however, matter which other site we choose so long as there is a finite p value attached to it and we will in all such cases get the same relaxation time τ_{\dagger} appropriate to the mode.

The relaxation times under the total symmetric oscillation are ∞ and

$$\frac{1}{\left(8\frac{K}{a} + 2Ka\right)}.$$

It may be seen that if $Ka = K/a = K$ we have $\tau = \infty$ and $1/10K$.

The relaxation times for the modes under E_g which are mechanically active are given by

$$\tau = \frac{\left(2Ka + \frac{8K}{a} + 6K\right) \pm \sqrt{\left(2Ka + \frac{8K}{a} + 6K\right)^2 - 4\left(12K^2a^2 + \frac{48K^2}{a^2}\right)}}{2\left(12K^2a^2 + \frac{48K^2}{a^2}\right)}.$$

If $K/a = Ka = K$ we obtain

$$\tau = \frac{1}{10K} \quad \text{or} \quad \frac{1}{6K}.$$

Under the F_{1u} mode, the relaxation time is

$$\tau = \frac{1}{6K + 2Ka}$$

and under F_{2u} the relaxation time is

$$\tau = \frac{1}{2Ka + 2K}.$$

Here again if $Ka = K/a = K$ we have $\tau = (1/8K)$ and $1/4K$ respectively.

4. DISCUSSION

In the case of simultaneous occurrence of two vacancies in the six available sites, besides a total symmetric mode which is mechanically active, we have one electrically active mode F_{2u} and three mechanically active modes, two under E_g and one under F_{2g} . Besides these, we have one mode in F_{1u} which is neither mechanically nor electrically active. On the other hand, in the case where only one vacancy is present, besides the trivial total symmetric mode, we should expect one electrically active

mode and one mechanically active mode only. Experimental results in the two cases may thus be expected to be quite different from each other.

It may also be pointed out that although the case studied in the present paper relates to the presence of 6 f.n. sites only, the method described can be extended to more complicated cases like KCl, etc., where a trivalent impurity is doped and the two vacancies created had been chance of simultaneously occupying any two of the 12 f.n. sites.

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REFERENCES

1. Bhagavantam, S. and Pantulu, P. V. *Proc. Ind. Acad. Sci.*, 1963, **58**, 183.
2. Dreyfus, R. W. .. *Phys. Rev.*, 1961, **121**, 1675.
3. Haven, Y. and Van Santen, J. H. *J. Chem. Phys.*, 1954, **22**, 1146.
4. Wachtman, Jr., J. B. .. *Phys. Rev.*, 1963, **131**, 517.