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 Pr³⁺ introduced substitutionally.

1. INTRODUCTION

The study of dielectric and mechanical relaxation due to point defects in crystals has attracted considerable attention in recent times. 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 neighborhood 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 shown 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 (Pr³⁺) 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 neighbor (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 $(\alpha \beta)$.

![Diagram of an octahedron with labeled sites and pairs](image-url)

We assume that a vacancy can jump only to one of the four nearest 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 $K\alpha$ for such a jump. The return jump (13)--(12) is made with frequency $K/\alpha$. $\alpha$ is an arbitrary constant. We neglect simultaneous jumps like 1–4 and 2–3 which change (12)--(34).