

Impurity Modes and Effective Force Constant in CsCl

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A theoretical study of the localized modes due to H^- and D^- (U centers) impurity ions and of the gap mode due to the K^+ ion in CsCl has been made. The values of the effective force constant have been determined in different frequency regions. The values are seen to be strikingly similar in magnitude in all frequency regions.

I. INTRODUCTION

Many theoretical and experimental investigations have been undertaken in recent years to understand the physical properties of ionic crystals doped with impurities. Invariably, in all the theoretical studies a nearest-neighbor perturbation model for the impurity has been assumed. Changes in the force constants between the impurity and its neighbors have been determined to explain the infrared absorption spectra of the doped solids. In order to give a physical meaning to perturbations of short-range type, it is necessary to evolve an idea of a force constant having short range, i. e., an effective force constant in the pure crystal. The reason is that in the rigid-ion picture of the lattice the assumption of short-range interactions presents no conceptual difficulty. However in the shell model or the deformation-dipole model of the lattice, where along with short-range hard-core repulsive forces there exist long-range dipolar forces in the ionic crystals, the situation is different.

In an earlier paper¹ we defined an effective force constant in the rigid-ion picture of the lattice. A theoretical study of infrared lattice absorption in CsI crystals containing impurities has been made by the authors.² The values of the effective force constant for CsI in different frequency regions have also been determined.^{3,4}

In the present communication we have made a theoretical study of the U -center localized modes and the gap mode due to K^+ observed in CsCl crystals. The values of the effective force constant in different frequency regions have been obtained.

II. CALCULATIONS AND RESULTS

The impurities having much lighter mass than the host ions of the solid usually produce highly localized modes with frequencies higher than the maximum phonon frequencies of the lattice. If there exist gaps between the acoustic- and optic-polarization branches of vibrations of the crystal, the localized modes may appear in a gap and they are called gap modes. Dötsch and Mitra⁵ have

observed highly localized modes in the far infrared due to U centers (H^- and D^-) in cesium halides.

Recently Becker⁶ had detected a gap mode in the infrared measurements of CsCl doped with K^+ . The frequencies of such infrared-active localized modes are determined by^{1,3}

$$\text{Re}D_{F_{1u}}(z) = 0, \quad (1)$$

where

$$D_{F_{1u}}(z) = (1 - \epsilon\omega^2g_1^\pm) \left[1 + \frac{1}{3}\chi\lambda(3g_1^\mp + 2g_4^\pm - g_5^\pm - 2g_6^\pm + 3g_7^\pm + 6g_8^\pm - g_9^\pm + 2g_{10}^\pm) \right] + \frac{8}{3}\lambda \left[g_1^\pm - 2\chi^{1/2}(g_2 + 2g_3^\pm) + \chi\epsilon\omega^2(g_2 + 2g_3^\pm)^2 \right] \quad (2)$$

for a crystal having CsCl structure. The different Green's functions occurring in Eq. (2) have been defined earlier.³ Here $\chi = M_\pm/M_*$ is the ratio of the masses of the two host ions in a unit cell; $\epsilon = \Delta M/M_\pm$ is the mass-change parameter and $\lambda = \gamma/M_\pm$ represents the change in the nearest-neighbor central force constant γ . The upper and lower signs (\pm) on the g 's and M are for the positive and the negative impurity, respectively. In Eq. (2) we have considered changes in the central forces only. The change in the noncentral force constants are usually seen to be smaller by an order of magnitude than the central ones in the ionic crystals.

After introducing the effective force constant, the resonance denominator simplifies to³

$$D_{F_{1u}}(z) = (1 + \beta)(1 - \epsilon\omega^2g_1^\pm) + 3\beta(1 + \epsilon)(\omega^2/8\eta) \times (1 + \omega^2g_1^\pm), \quad (3)$$

where $\eta = \gamma/M_\pm$ and $\beta = \lambda/\eta$ is the relative change in the force constant. Equation (2) can be used to determine the change in the force constant in the nearest-neighbor perturbation model. One can then determine the nearest-neighbor effective force constant by using Eq. (3).

In order to calculate the lattice response functions appearing in Eq. (2), the necessary data for eigenfrequencies and eigenvectors of CsCl obtained

by Mahler and Engelhard⁷ at 4.2 °K using the breathing-shell model has been used. A mesh of 2744 points distributed uniformly in the Brillouin zone has been chosen in this calculation.

The whole frequency range is divided into 60 equal bins and histograms corresponding to each Green's function matrix elements are calculated at the center of each bin. The histograms are employed to calculate the Green's functions below the maximum frequency of the crystal and above it. A finite value 0.4 in units of bin width for the frequency increment in the integration was found to be appropriate in order to minimize the spurious fluctuations which occur in the Green's functions. The maximum phonon frequency of CsCl as given by Mahler's calculation is 3.13684×10^{13} rad/sec.

Using the calculated values of the Green's functions the force constant change, λ , is evaluated with the help of Eq. (1). This value of λ is used to evaluate the effective force constant $\frac{8}{3}\eta$ using Eq. (3). Apart from this the force constant is determined using zero-frequency resonance. The results for three systems, i. e., CsCl:K⁺, CsCl:H⁻, and CsCl:D⁻, are presented in Table I along with the frequencies of the localized modes used in the calculations. In Table II we present the effective force constant in the three different frequency regions, i. e., the low-frequency region, the gap region, and the high-frequency region. In the low-frequency region, the effective force constant has been determined by zero-frequency resonance, whereas in the gap and the high-frequency regions, they are determined by localized-mode frequencies. The values obtained by Benedek and Nardelli⁸ in the low-frequency region in the framework of Hardy's deformation-dipole model have also been shown in Table II. The results for CsI obtained earlier⁴ are also included in Table II for the sake of completeness.

III. DISCUSSION

From Table I, we observe that the relative change in the effective force constants due to K⁺, H⁻, and D⁻ impurity ions in CsCl are about 55%. The

TABLE I. Column two lists the localized-mode frequencies, column three the changes in the nearest-neighbor force constant, column four the values of the effective force constant, and column five the relative changes in the force constant in CsCl.

Impurity ion	ω_L (10^{13} rad/sec)	$\frac{8}{3}\lambda$ (10^{26} sec ⁻²)	$\frac{8}{3}\eta$ (10^{26} sec ⁻²)	β
K ⁺	1.616 ^a	-1.054	1.998	-0.53
H ⁻	8.006 ^b	-2.116	3.935	-0.55
D ⁻	5.683 ^b	-2.274	4.103	-0.56

^aReference 6.

^bReference 5.

TABLE II. Effective force constant in different frequency regions in CsCl and CsI crystals in units of 10^4 g sec⁻².

Crystal	Low frequency			Gap region ^b	High frequency ^b
	Ref. a	Ref. b	Ref. c		
CsCl	2.388	4.409	...
	2.466	...	2.454	...	2.316 (H ⁻) 2.415 (D ⁻)
CsI	2.250	2.141 (In ⁺) 2.030 (Γ ⁺)	1.970
	2.002	1.460 (H ⁻) 1.669 (D ⁻)

^aBy $\omega_R = 0$.

^bUsing Eqs. (1)–(3).

^cValues obtained in Hardy's deformation-dipole model (Ref. 8).

changes in the effective force constants for the two isotopes of hydrogen are approximately the same. The difference in the values of λ lie within 8%. It supports the isotopic character of the two impurity ions H⁻ and D⁻. But the same is not true in the case of CsI. The difference in the two values of λ incurred by H⁻ and D⁻ impurity ions was not seen to be small but was as large as 20%.

From Table II, we note that the values of the effective force constants for the CsCl crystal are strikingly similar in the high- and the low-frequency regions. The value obtained by Benedek and Nardelli in the framework of Hardy's deformation-dipole-lattice model is also very near to these values. The value of the force constant due to the gap mode (85.8 cm⁻¹) in the gap region is unexpectedly high. It may occur because of the fact that the gap region seen in the calculations of Mahler and Engelhard lies at higher frequencies, i. e., 87–97 cm⁻¹, than the observed minimum (76–88 cm⁻¹) in the experimental measurement of infrared absorption in CsCl.⁶ The calculations of the breathing-shell model performed by Mahler and Engelhard need to be improved; especially for the high-frequency phonons. In the case of CsI, the values of the effective force constant in the high-frequency region are smaller than those of the low-frequency region; the difference is of the order of 20–30%.

Note added in proof. Recently the authors have successfully reproduced the experimentally observed infrared absorption in CsCl:K⁺ by considering the changes in the central and the noncentral interactions (unpublished). The modified value of the effective force constant is seen to be 2.194×10^4 g sec⁻², which is quite near to its value in the low- and the high-frequency regions.

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X-Ray Study of Anharmonic Vibrations in Calcium Fluoride[†]

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From temperature-dependent x-ray integrated intensity measurements on single crystals of calcium fluoride, we have demonstrated the presence of anharmonic fluorine-atom vibrations. For the cubic term in the single-particle fluorine potential we arrive at a value of $\beta = -(4.5 \pm 1.5) \times 10^{-12}$ erg/Å³. The experimentally determined temperature factors at 25 °C are $B_{Ca} (= 8\pi^2 \langle \mu_C^2 \rangle_{Ca}) = 0.525 \pm 0.01$ Å² and $B_F = 0.787 \pm 0.03$ Å².

INTRODUCTION

The results of a detailed temperature-dependent x-ray investigation of calcium fluoride are presented in this paper. Our objective was to use x-ray diffraction methods to observe and quantitatively measure the anharmonic anisotropic thermal vibrations in calcium fluoride.

Using neutron diffraction techniques, Willis¹ observed different temperature dependences for the integrated neutron intensities from three calcium fluoride Bragg reflections [(755), (771), (933)] occurring at the same $(\sin\theta)/\lambda$ value. Since CaF₂ is cubic, the observation of anisotropic temperature factors was unexpected and is in violation of harmonic-theory predictions. Willis, however, was able to quantitatively explain his observations using a phenomenological model based on anharmonic fluorine-ion vibrations.

These original experiments and the interpretation of the results met with considerable criticism by Ladell,² Hamilton,³ and Pryor.⁴ Later neutron work, however, by Willis and his co-workers at Harwell on BaF₂,⁵ and on UO₂,⁶ firmly established the existence of systematic anisotropic diffraction effects from compounds having the fluorite structure.

Only recently were similar effects observed in x-ray data (CaF₂ by Cooper⁷ and Mg₂Si by Cooper and Panke⁸). This time lag was primarily due to the unfavorable anion-to-cation scattering-factor ratio that exists for x rays, making anharmonicity

effects small and difficult to observe. In the present study, anharmonicity effects were made quite substantial by limiting observations to high-index reflections at elevated temperatures. Further, we feel we have eliminated a main objection to the earlier work, viz., extinction, by mechanically deforming the samples.

Anharmonic effects in x-ray diffraction are in some cases coupled with anisotropic bonding charge distributions. In a recent coupled x-ray⁹ and neutron¹⁰ experiment on silicon, both bonding and anharmonic contributions to the (222) forbidden reflection in silicon were measured. Such covalency effects were assumed to be negligible in calcium fluoride because of its ionic character. As a consequence, only the anharmonicity portion of the antisymmetric electron density distribution was considered in our data analysis.

THEORY

Calcium fluoride has the fluorite structure; see Fig. 1. It can be constructed on a face centered cubic lattice using a three-atom basis, one cation at the origin and two anions, one each located at plus and minus $\frac{1}{4} \frac{1}{4} \frac{1}{4}$. The calcium atoms are coordinated to eight fluorine atoms located at the corners of the outlined cube (*m3m* symmetry). Only half of these unit fluorine cubes have a calcium at their body center, the other half are empty. The fluorine atoms are coordinated to four calcium atoms located at the corners of a regular tetra-