Phonon resonances associated with a vacancy in CaF_2

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A Green-function formulation for calculating the phonon resonances due to an anion vacancy in CaF_2 is given. From a study of the relaxations of the first and second neighbors of an anion vacancy in CaF_2, we have computed the force-constant changes, felt by these first and second neighbors due to the anion vacancy. These force-constant changes along with the lattice Green function of CaF_2 (computed from shell-model data fitted to the experimental phonon dispersion curves) are employed to estimate the potential resonant modes in this system. Symmetry coordinates are used to block diagonalize the g and δl matrices and hence to study the resonant modes occurring under the different individual irreducible representations. Resonant modes are predicted under the A, F_1, and F_2 representations. The possibility of detecting some of these modes experimentally is discussed.

I. INTRODUCTION

When a vacancy is introduced into the crystal, either by the removal of an atom from the host lattice or by introducing aliovalent impurities substitutionally in an ionic crystal with the vacancy being formed to conserve electroneutrality, the neighboring host atoms of this vacancy undergo sizeable readjustments in their equilibrium positions due to the sudden weakening of the interaction felt by them when the vacancy is formed. In CaF_2 crystals, where Frenkel defects happen to be the major defects responsible for transport properties, vacancies are present to a sizeable extent. Further, for example, when a Na^+ ion is substituted in the Ca^{2+} site, the charge compensation is achieved by the presence of an anion vacancy. Langeler and Ludwig[1] studied the vacancy in a simple cubic lattice and showed that local modes do not exist there due to a vacancy. The next detailed investigation on vibrational effects due to vacancies was by Land and Goodman[2] who considered the case of cubic metals with short-range forces. Due to the force-constant weakening experienced over a large number of neighbors, in their work they had to resort to a molecular calculation without the use of lattice Green functions. Their study revealed the existence in Cu of a vacancy-induced mode slightly above the continuum, which they regarded as the local mode. Nardelli and Terzi[3] have investigated the vacancy in fcc argon and have evaluated the entropy of formation of a vacancy, both without relaxation and including an elastic relaxation. Krumhansal[4] has discussed the role of phonon resonances due to a vacancy in a crystal in thermal conductivity. Impurity modes due to vacancies in ionic crystals have not been investigated in detail, probably because until recently methods of evaluating the lattice relaxation in a self-consistent way had not been developed. Since a fairly-well-tested lattice potential is available for CaF_2 from the work of Catlow and Norgett[5] and lattice-relaxation calculations can be carried out accurately using the HADES program developed by Norgett,[6] we thought it worthwhile to examine the impurity modes, especially the phonon resonances, associated with an isolated vacancy in CaF_2 using the lattice Green-function approach. The availability of neutron scattering results[7] on the phonon dispersion relation in CaF_2 enables one to compute these Green functions fairly accurately. In Sec. II we shall briefly outline the theory we have employed and apply this to a vacancy at an anion site in CaF_2. Details on the symmetry coordinates which simplifies the problem

considerably are given in Sec. III. The details on the calculation of Green-function and force-constant parameters are given in Sec. IV and our results on the phonon resonances are given in Sec. V. Finally we shall discuss the results, state the conclusions arising out of these studies, and also look at the possibilities of observing some of these resonant modes experimentally. Since the general theory is quite similar to the one discussed in an earlier paper for the interstitial[8] we shall hereafter refer to this as Paper I.

II. THEORY OF DEFECT MODES FOR VACANCY, APPLIED TO CaF_2

Since the basic theory of impurity modes is discussed in detail elsewhere,[8–10] we shall mention only a few important aspects which are relevant to the present problem. The vacancy is taken at the origin and the presence of the vacancy is felt only by a few neighbors surrounding it; the remaining atoms of the host crystal are assumed to be unperturbed. If m atoms, including the site of the vacancy, are included in this so called "defect space", the impurity modes are obtainable from the condition that the determinant

$$|I - \underline{g}(\omega)\delta\underline{l}(\omega)| = 0 \quad . \tag{1}$$

$\underline{g}(\omega)$ is the lattice Green functions of the host crystal in the three m-dimensional defect space. $\delta\underline{l}(\omega)$ is the perturbation arising from the mass change and force-constant changes and is defined by

$$\delta l_{\alpha\beta}(\omega) = \epsilon m\omega^2\delta_{KK'}\delta_{\alpha\beta} + [\phi_{\alpha\beta}(KK') - \Phi^0_{\alpha\beta}(KK')] \quad , \tag{2}$$

where the first term arises from the mass change at the origin when a vacancy is formed. $[\phi_{\alpha\beta}(KK') - \phi^0_{\alpha\beta}(KK')]$ is the matrix element for the change in force constants felt between atoms K and K' with the superscript 0 representing the host crystal. ϵ the mass defect parameter is defined as

$$\epsilon = \frac{M_{\text{host atom}} - M_{\text{defect atom}}}{M_{\text{host atom}}} \tag{3}$$

and is unity in the case of a vacancy. The important point to note is that the formation of a vacancy by removal of an atom to ∞ removes 3 degrees of freedom from the crystal and hence in evaluating the effects of vacancy on the crystal properties which are dependent in Eq. (1), we should make suitable truncations in g and δl corresponding to the vacancy degrees of freedom.

Let us now apply these basic principles to the CaF_2 lattice which has three interpenetrating fcc sublattices corresponding to Ca^{2+}, $F^-_{(1)}$, and $F^-_{(2)}$ ions. If we take a $F^-_{(1)}$ ion site as the origin and remove this $F^-_{(1)}$ ion

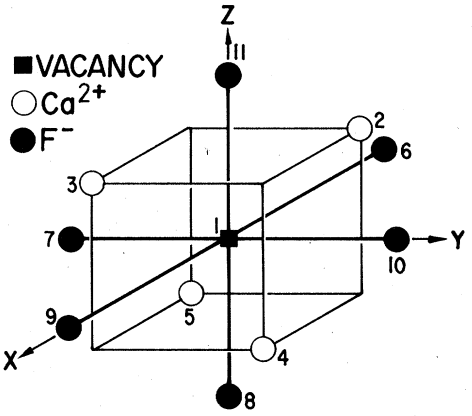

FIG. 1. Anion vacancy and its first and second neighbors in CaF_2.

to create a vacancy, this vacancy is surrounded by four Ca^{2+} ions as nearest neighbors and six $F^-_{(2)}$ ions as second neighbors (see Fig. 1). We shall assume that the further neighbors are unperturbed by the vacancy. This assumption is made partly to make the defect space (33×33) amenable for calculations, and partly from our experience (which we shall discuss later in the paper) of the relaxations of the various neighbors obtained from the Catlow and Norgett potential.[5] We shall give below the atom labeling and the coordinates of the atoms in units of a_0, the $F_{(1)} - F_{(2)}$ distance.

Atom number	Atom type	Coordinates
1	Vacancy (at $F^-_{(1)}$ site)	0 0 0
2	Ca^{2+}	$\frac{\bar{1}}{2}\ \frac{1}{2}\ \frac{1}{2}$
3	Ca^{2+}	$\frac{1}{2}\ \frac{\bar{1}}{2}\ \frac{1}{2}$
4	Ca^{2+}	$\frac{1}{2}\ \frac{1}{2}\ \frac{\bar{1}}{2}$
5	Ca^{2+}	$\frac{\bar{1}}{2}\ \frac{\bar{1}}{2}\ \frac{\bar{1}}{2}$
6	$F^-_{(2)}$	$\bar{1}\ 0\ 0$
7	$F^-_{(2)}$	$0\ \bar{1}\ 0$
8	$F^-_{(2)}$	$0\ 0\ \bar{1}$
9	$F^-_{(2)}$	$1\ 0\ 0$
10	$F^-_{(2)}$	$0\ 1\ 0$
11	$F^-_{(2)}$	$0\ 0\ 1$

A perusal of the above coordinates and the symmetry associated with the various lattice Green-function matrix elements for atoms 1 to 11 above shows that the following 21 Green-function matrix elements alone are sufficient to express the g matrix in Eq. (1). These Green-function matrix ele-

ments are given below, each one with an alphabetical label for convenience of discussion. We have followed the notational features of Lacina and Pershan[11] as far as possible.

$$g_{xx}\begin{pmatrix}0-0\\F_{(1)}-F_{(1)}\end{pmatrix}=g_{xx}\begin{pmatrix}0-0\\F_{(2)}-F_{(2)}\end{pmatrix}=B,$$

$$g_{xx}\begin{pmatrix}0-100\\F_{(1)}-F_{(1)}\end{pmatrix}=P\ ,\quad g_{xx}\begin{pmatrix}0-0\\Ca-Ca\end{pmatrix}=A_1,$$

$$g_{xy}\begin{pmatrix}0-110\\F_{(1)}-F_{(1)}\end{pmatrix}=R\ ,\quad g_{xx}\begin{pmatrix}0-\frac{1}{2}\frac{1}{2}\frac{1}{2}\\F_{(1)}-Ca\end{pmatrix}=Y,$$

$$g_{xz}\begin{pmatrix}0-110\\F_{(1)}-F_{(1)}\end{pmatrix}=S\ ,\quad g_{xy}\begin{pmatrix}0-\frac{1}{2}\frac{1}{2}\frac{1}{2}\\F_{(1)}-Ca\end{pmatrix}=Z,$$

$$g_{zz}\begin{pmatrix}0-110\\F_{(1)}-F_{(1)}\end{pmatrix}=Q\ ,\quad g_{xx}\begin{pmatrix}0-100\\F_{(1)}-F_{(2)}\end{pmatrix}=F,$$

$$g_{xx}\begin{pmatrix}0-\frac{3}{2}\frac{1}{2}\frac{1}{2}\\Ca-F_{(2)}\end{pmatrix}=C_1\ ,\quad g_{yy}\begin{pmatrix}0-100\\F_{(1)}-F_{(2)}\end{pmatrix}=M,$$

$$g_{yx}\begin{pmatrix}0-\frac{3}{2}\frac{1}{2}\frac{1}{2}\\Ca-F_{(2)}\end{pmatrix}=E_1\ ,\quad g_{yz}\begin{pmatrix}0-100\\F_{(1)}-F_{(2)}\end{pmatrix}=H,$$

$$g_{yz}\begin{pmatrix}0-\frac{3}{2}\frac{1}{2}\frac{1}{2}\\Ca-F_{(2)}\end{pmatrix}=J_1\ ,\quad g_{xx}\begin{pmatrix}0-110\\Ca-Ca\end{pmatrix}=P_1,$$

$$g_{yy}\begin{pmatrix}0-\frac{3}{2}\frac{1}{2}\frac{1}{2}\\Ca-F_{(2)}\end{pmatrix}=G_1\ ,\quad g_{xy}\begin{pmatrix}0-110\\Ca-Ca\end{pmatrix}=R_1,$$

$$g_{xx}\begin{pmatrix}0-200\\F_{(2)}-F_{(2)}\end{pmatrix}=A_3\ ,\quad g_{zz}\begin{pmatrix}0-110\\Ca-Ca\end{pmatrix}=Q_1,$$

$$g_{yy}\begin{pmatrix}0-200\\F_{(2)}-F_{(2)}\end{pmatrix}=B_3\ ,\quad g_{xy}\begin{pmatrix}0-\frac{3}{2}\frac{1}{2}\frac{1}{2}\\Ca-F_{(2)}\end{pmatrix}=D_1\ . \tag{4}$$

In terms of these matrix elements the 33×33 g matrix is shown in Table I.

We shall represent the matrix for the force-constant changes between the vacancy and the nearest neighbor Ca^{2+} (atom 2 for example) as

$$\Delta\phi(1-2)=-\begin{pmatrix}\Delta A_1 & -\Delta B_1 & -\Delta B_1\\ -\Delta B_1 & \Delta A_1 & \Delta B_1\\ -\Delta B_1 & \Delta B_1 & \Delta A_1\end{pmatrix}, \tag{5}$$

where $\Delta A_1=\frac{1}{3}(\Delta A+2\Delta B)$ and

$$\Delta B_1=\tfrac{1}{3}(\Delta A-\Delta B)\ . \tag{6}$$

ΔA and ΔB are the changes in the respective Kellermann parameters[12] A and B defined as

$$A=\left(\frac{\partial^2\phi}{\partial r^2}\right)_{\text{equilibrium}}\ ,\quad B=\left(\frac{1}{r}\frac{\partial\phi}{\partial r}\right)_{\text{equilibrium}}\ . \tag{7}$$

$\Delta\phi(1-3)$, $\Delta\phi(1-4)$, and $\Delta\phi(1-5)$ are obtainable from $\Delta\phi(1-2)$ by symmetry. Similarly for the second neighbors (say atom 6) one can write

$$\Delta\phi(1-6)=\begin{pmatrix}\Delta A_2 & 0 & 0\\ & \Delta B_2 & \\ 0 & 0 & \Delta B_2\end{pmatrix}, \tag{8}$$

where ΔA_2 and ΔB_2 are the changes in Kellermann's parameters A and B defined in a similar way for the second-neighbor interaction. $\Delta\phi(1-7)$ to $\Delta\phi(1-11)$ can be obtained from $\Delta\phi(1-6)$ using symmetry.

However, when the vacancy is introduced, atom 2 relaxes to a new equilibrium position and so do the other host atoms in the defect space. Accordingly even the interactions among these host atoms become altered. In the present calculations such changes among the nearest neighbors are taken into account through the parameters ΔC_1 and ΔD_1 which are very similar in form to ΔA_1 and ΔB_1 defined above. In terms of these parameters, the δl matrix (33×33) is written as shown in Table II.

III. SYMMETRY COORDINATES

The vacancy site has T_d symmetry and the 33-dimensional defect space can be expressed in terms of the various irreducible representations of T_d as

$$\Gamma_{33}=2A+2E+3F_1+6F_2\ .$$

Standard projection operator method of group theory is used to work out the symmetry coordinates which can be used to block diagonalize both the g and δl matrices. One gets a 2×2 block for A, a 2×2 block for E, a 3×3 block for $F_{(1)}$, and a 6×6 block for the $F_{(2)}$ representations. For the $F_{(2)}$ representation we select such a set of orthornormal symmetry coordinates that not only decouple the X, Y, and Z components, but also make the translational motion apparent, especially in the δl matrix in the zero-frequency limit. We also see that one of the $F_{(2)}$ modes becomes uncoupled from the others. (We shall call this $F'_{(2)}$ for convenience). Hence the other $F_{(2)}$ blocks as a whole constitute a 5×5 matrix. The symmetry coordinates used here can be obtained from those given by Brice[13] for the interstitial in Si and hence they are not repeated here.

TABLE I. g matrix. This matrix is symmetric.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
1	B	0	0	Y	$-Z$	$-Z$	Y	$-Z$	Z	Y	Z	$-Z$	Y	Z	Z	F	0	0	M	0	$-H$	M	$-H$	0	F	0	0	0	M	0	H	M	H	0
2		B	0	$-Z$	Y	Z	$-Z$	Y	$-Z$	Z	Y	$-Z$	Z	Z	Y	0	M	$-H$	M	$-H$	0	F	0	$-H$	M	0	0	M	H	0	F	0	H	M	0
3			B	$-Z$	Z	Y	$+Z$	$-Z$	Y	$-Z$	$-Z$	Y	Z	Z	Y	0	Y	Z	M	$-H$	M	0	M	0	F	0	H	M	H	0	M	0	0	F
4				A_1	0	0	P_1	$-R_1$	0	P_1	0	$-R_1$	Q_1	0	0	Y	Z	Z	G_1	$-E_1$	$-J_1$	G_1	$-J_1$	$-E_1$	C_1	$-D_1$	$-D_1$	Y	Z	$-Z$	Y	$-Z$	Z
5					A_1	0	$-R_1$	P_1	0	$-R_1$	Q_1	0	0	P_1	R_1	Z	Z	Y	$-D_1$	C_1	D_1	$-J_1$	G_1	E_1	$-E_1$	G_1	J_1	Z	Y	$-Z$	$-Z$	Y	$-Z$
6						A_1	0	0	Q_1	$-R_1$	0	P_1	0	R_1	P_1	Z	Z	Y	$-J_1$	E_1	G_1	$-D_1$	D_1	C_1	E_1	Y	Z	$-Z$	G_1	$-E_1$	J_1	Y	Z	$-Z$	Y
7							A_1	0	0	Q_1	0	0	P_1	0	R_1	C_1	$-D_1$	D_1	Y	Z	Z	G_1	$-J_1$	E_1	Y	Z	$-Z$	G_1	$-E_1$	J_1	Y	$-Z$	$-Z$
8								A_1	0	0	P_1	$-R_1$	0	Q_1	0	$-E_1$	G_1	$-J_1$	Z	Y	Z	$-J_1$	G_1	$-E_1$	Z	Y	Z	$-Z$	$-D_1$	C_1	$-D_1$	$-Z$	Z
9									A_1	0	$-R_1$	P_1	R_1	0	P_1	E_1	$-J_1$	G_1	Z	Z	Y	D_1	$-D_1$	C_1	$-Z$	$-Z$	J_1	$-E_1$	G_1	$-Z$	Z	Y
10										A_1	0	0	P_1	R_1	0	C_1	D_1	$-D_1$	G_1	E_1	$-J_1$	Z	Y	Z	Y	$-Z$	Z	$-Z$	G_1	J_1	$-E_1$
11											A_1	0	R_1	P_1	0	E_1	G_1	$-J_1$	D_1	C_1	$-D_1$	Z	Y	Z	$-Z$	Y	$-Z$	$-Z$	Y	J_1	G_1	$-E_1$
12												A_1	0	0	Q_1	$-E_1$	$-J_1$	G_1	$-J_1$	$-E_1$	G_1	Z	Z	Y	Z	$-Z$	Y	$-Z$	Z	Y	$-D_1$	$-D_1$	C_1
13													A_1	0	0	Y	$-Z$	$-Z$	Y	$-Z$	Z	Y	Z	C_1	D_1	D_1	G_1	E_1	J_1	G_1	J_1	E_1
14														A_1	0	$-Z$	Y	Z	$-Z$	Y	$-Z$	Z	Y	$-Z$	E_1	G_1	J_1	D_1	C_1	D_1	J_1	G_1	E_1
15															A_1	$-Z$	Z	Y	Z	$-Z$	Y	$-Z$	Y	$-Z$	D_1	G_1	J_1	D_1	E_1	G_1	D_1	J_1	D_1	C_1
16																B	0	0	P	$-R$	S	P	S	$-R$	A_3	0	B_3	0	P	R	$-S$	P	$-S$	R
17																	B	0	$-R$	P	$-S$	$-S$	Q	S	0	B_3	0	R	P	$-S$	S	Q	S
18																		B	$-S$	S	$-R$	$-R$	$-S$	P	0	0	B_3	S	S	Q	R	$-S$	P
19																			B	0	Q	$-S$	P	S	P	R	Q	B_3	0	Q	S	P	S
20																				B	0	S	P	$-R$	R	P	$-S$	0	A_3	0	$-S$	P	R
21																					B	$-S$	Q	P	S	S	Q	$-S$	0	B_3	$-S$	R	P
22																						B	0	0	P	$-S$	R	Q	S	S	B_3	0	0
23																							B	0	S	Q	S	$-S$	P	R	0	B_3	0
24																								B	R	$-S$	P	$-S$	R	P	0	0	A_3
25																									B	0	0	P	$-R$	$-S$	P	$-S$	$-R$
26																										B	0	$-R$	P	S	S	Q	$-S$
27																											B	S	$-S$	Q	$-R$	S	P
28																												B	0	0	Q	S	$-S$
29																													B	0	$-S$	P	$-R$
30																														B	S	$-R$	P
31																															B	0	0
32																																B	0
33																																	B

TABLE II. δI matrix, where $\Delta E_1 = -\Delta A_1 - 3\Delta C_1$; $\Delta F_1 = \Delta B_1 - \Delta D_1$; $\Delta G_1 = -\Delta A_2 - 2\Delta C_1$; $\Delta H_1 = -\Delta B_2 - 2\Delta C_1$; $\Delta I_1 = -2\Delta D_1$; $D_1 = -4\Delta A_1 - \Delta A_2 - 2\Delta B_2 + \epsilon m\omega^2$. This matrix is symmetric.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
1	D_1	0	0	ΔA_1	$-\Delta B_1$	$-\Delta B_1$	ΔA_1	$-\Delta B_1$	ΔB_1	ΔA_1	ΔB_1	$-\Delta B_1$	ΔA_1	ΔB_1	ΔB_1	ΔA_2	0	0	ΔB_2	0	0	ΔB_2	0	0	ΔA_2	0	0	ΔB_2	0	0	ΔB_2	0	0
2		D_1	0	$-\Delta B_1$	ΔA_1	ΔB_1	$-\Delta B_1$	ΔA_1	$-\Delta B_1$	ΔB_1	ΔA_1	$-\Delta B_1$	ΔB_1	ΔA_1	ΔB_1	0	ΔB_2	0	0	ΔA_2	0	0	ΔB_2	0	0	ΔB_2	0	0	ΔA_2	0	0	ΔB_2	0
3			D_1	$-\Delta B_1$	ΔB_1	ΔA_1	ΔB_1	$-\Delta B_1$	ΔA_1	$-\Delta B_1$	$-\Delta B_1$	ΔA_1	ΔB_1	ΔB_1	ΔA_1	0	0	ΔB_2	0	0	ΔB_2	0	0	ΔA_2	0	0	ΔB_2	0	0	ΔB_2	0	0	ΔA_2
4				ΔE_1	$-\Delta F_1$	$-\Delta F_1$										ΔC_1	ΔD_1	ΔD_1										ΔC_1	ΔD_1	$-\Delta D_1$	ΔC_1	$-\Delta D_1$	ΔD_1
5					ΔE_1	ΔF_1		0			0			0		ΔD_1	ΔC_1	ΔD_1		0			0			0		ΔD_1	ΔC_1	$-\Delta D_1$	$-\Delta D_1$	ΔC_1	ΔD_1
6						ΔE_1										ΔD_1	ΔD_1	ΔC_1										$-\Delta D_1$	$-\Delta D_1$	ΔC_1	ΔD_1	$-\Delta D_1$	ΔC_1
7							ΔE_1	$-\Delta F_1$	ΔF_1										ΔC_1	ΔD_1	ΔD_1				ΔC_1	ΔD_1	$-\Delta D_1$				ΔC_1	$-\Delta D_1$	$-\Delta D_1$
8								ΔE_1	$-\Delta F_1$		0			0			0		ΔD_1	ΔC_1	ΔD_1		0		ΔD_1	ΔC_1	$-\Delta D_1$		0		$-\Delta D_1$	ΔC_1	ΔD_1
9									ΔE_1										ΔD_1	ΔD_1	ΔC_1				$-\Delta D_1$	$-\Delta D_1$	ΔC_1				$-\Delta D_1$	ΔD_1	ΔC_1
10										ΔE_1	ΔF_1	$-\Delta F_1$										ΔC_1	ΔD_1	ΔD_1	ΔC_1	$-\Delta D_1$	ΔD_1	ΔC_1	$-\Delta D_1$	$-\Delta D_1$			
11											ΔE_1	$-\Delta F_1$		0			0			0		ΔD_1	ΔC_1	ΔD_1	$-\Delta D_1$	ΔC_1	$-\Delta D_1$	$-\Delta D_1$	ΔC_1	ΔD_1		0	
12												ΔE_1										ΔD_1	ΔD_1	ΔC_1	ΔD_1	$-\Delta D_1$	ΔC_1	$-\Delta D_1$	ΔD_1	ΔC_1			
13													ΔE_1	ΔF_1	ΔF_1	ΔG_1	$-\Delta D_1$	$-\Delta D_1$	ΔC_1	$-\Delta D_1$	ΔD_1	ΔC_1	ΔD_1	ΔD_1									
14														ΔE_1	ΔF_1	$-\Delta D_1$	ΔC_1	ΔD_1	$-\Delta D_1$	ΔC_1	$-\Delta D_1$	ΔD_1	ΔC_1	$-\Delta D_1$		0			0		0	
15															ΔE_1	$-\Delta D_1$	ΔD_1	ΔC_1	ΔD_1	$-\Delta D_1$	ΔC_1	$-\Delta D_1$	$-\Delta D_1$	ΔC_1								
16																ΔG_1	0	0															
17																	ΔH_1	ΔI_1		0			0			0			0			0	
18																		ΔH_1															
19																			ΔH_1	0	ΔI_1											
20																				ΔG_1	0		0			0			0			0	
21																					ΔH_1											
22																						ΔH_1	ΔI_1	0								
23																							ΔH_1	0		0			0			0	
24																								ΔG_1									
25																									ΔG_1	0							
26																										ΔH_1	$-\Delta I_1$		0			0	
27																											ΔH_1						
28																												ΔH_1	0	$-\Delta I_1$		0	
29																													ΔG_1	0			
30																														ΔH_1			
31																															ΔH_1	$-\Delta I_1$	0
32																																ΔH_1	0
33																																	ΔG_1

IV. EVALUATION OF GREEN-FUNCTION MATRIX ELEMENTS

The phonon frequencies and eigenvectors computed on the basis of a shell model the parameters of which had been fitted to the experimental phonon dispersion data of Elcombe and Pryor[7] have been used to compute the Green functions. The details of these calculations are available from the work of Krishnamurthy and Haridasan[14] and from Paper I. These Green functions are obtained for $(\omega/\omega_L = x)$ ranging from 0.01 to 0.99 at intervals of 0.02.

A. Evaluation of force-constant parameters

As in Paper I we employ the Catlow-Norgett potential for CaF_2 [model (i)] in conjunction with the HADES program to compute the relaxations of the nearest-neighbor Ca^{2+} ions and second-neighbor $F^-_{(2)}$ ions. As one expects, an outward relaxation for Ca^{2+} ions and an inward relaxation for the $F^-_{(2)}$ ions occur. The actual relaxations computed are given below in terms of fractional coordinates for atoms 5 and 9, for example.

	Coordinates before relaxation	Relaxed coordinates
Atom 5	$(-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$	(−0.533, −0.533, −0.533)
Atom 9	(1,0,0)	(0.907,0,0)

The relaxation experienced by further neighbors are quite small, thereby justifying our present choice of the defect space.

With these relaxations known, the parameters ΔA_1, ΔB_1, ΔA_2, ΔB_2, ΔC_1, and ΔD_1 were evaluated using the Catlow and Norgett potential, in the same way as discussed in Paper I. In the case of a vacancy at anion site the following values are obtained for the parameters:

$$\Delta A_1 = 0.815 \times 10^4 \text{ dyn/cm} ,$$

$$\Delta B_1 = 2.9913 \times 10^4 \text{ dyn/cm} ,$$

$$\Delta A_2 = -0.5922 \times 10^4 \text{ dyn/cm} ,$$

$$\Delta B_2 = -0.2604 \times 10^4 \text{ dyn/cm} ;$$

set 1:

$$\Delta C_1 = -0.5192 \times 10^4 \text{ dyn/cm} ,$$

$$\Delta D_1 = -0.943 \times 10^4 \text{ dyn/cm} ;$$

set 2:

$$\Delta C_1 = -0.5192 \times 10^4 \text{ dyn/cm} ,$$

$$\Delta D_1 = -0.7831 \times 10^4 \text{ dyn/cm} ;$$

set 3:

$$\Delta C_1 = 0 ,$$

$$\Delta D_1 = 0 .$$

V. RESULTS

We have investigated the phonon resonances with three sets of data in all of which ΔA_1 to ΔB_2 are the same; (a) set 1 in which for ΔC_1 and ΔD_1 both the long-range and short-range contributions are accounted for; (b) set 2 in which for ΔC_1 and ΔD_1 only the short-range part is included; (c) set 3, where ΔC_1 and ΔD_1 are taken as zero.

The phonon resonances were tried by working out the real part of $(\underline{I} - \underline{g}\,\underline{\delta l})$, labeled as $\Delta_1^S(\omega)$ for the Sth representation, as a function of ω. The zeros of $\Delta_1^S(\omega)$ give the potential resonances whereas the width of the resonance is obtained by working out the imaginary part of the determinant, $\Delta_2^S(\omega)$. The width at the resonance frequency $\omega = \omega_R$ is given by $\Gamma = \{\Delta_2^S(\omega_R)/[\Delta_1^S(\omega_R)]'\}$ where the prime denotes differentiation with respect to ω. For a genuine resonance Γ should be negative and $|\Gamma| << \omega_L$. Further details are discussed in Paper I and by Maradudin *et al.*[15] We have evaluated Δ_1^S and Δ_2^S as functions of $x(=\omega/\omega_L)$ for each representation using the data of set 1, 2, and 3 and the Green functions. Figures 2 and 3 give the variations of Δ_1^S and Δ_2^S as functions of x, for the A representation. From these graphs we see possible resonant modes at $x = 0.62$ and 0.66 for set 1, but no such resonances for sets 2 and 3. However the corresponding Γ computed for $x = 0.62$ is positive, whereas it is negative and small for $x = 0.66$. Thus there is a resonant impurity mode of A_1 symmetry for the vacancy in CaF_2 at $x = 0.66$. No resonances occur under the E and F_2' symmetry species for all of the three models. On the other hand there is a resonance of F_1 symmetry around $x = 0.76$ for set 1 data with a corresponding Γ of −0.16. Set 2 data shows a likely resonance around that region

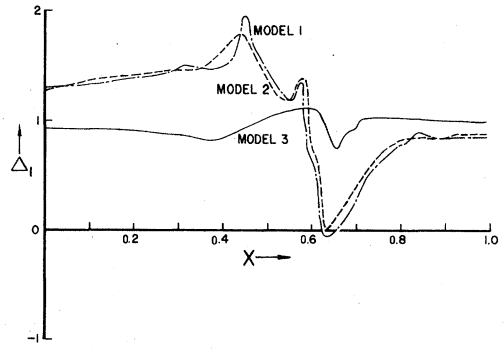

FIG. 2. Variation of Δ_1 with x for the A representation.

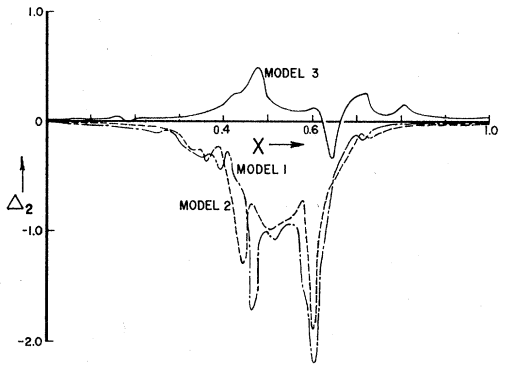

FIG. 3. Variation of Δ_2 with x for the A representation.

where the set 3 model does not predict any resonances at all.

Coming to the F_2 representation one finds possible resonances at $x=0.32$, 0.36, 0.62, and 0.70 for set 1, and $x=0.32$, 0.56, 0.70, and 0.72, for set 2 and at $x=0.32$, 0.62, 0.70, 0.72, and 0.84 for set 3. But the genuine resonances happen around $x=0.36$ and $x=0.62$ in set 1 and around $x=0.70$ for the other models. The corresponding Γ's for set 1 data are -0.083 and -0.030, respectively.

The set 1 results are taken to be the most reliable of the three since in that model ΔC_1 and ΔD_1 contain both the Coulomb and short-range contributions. Since the present calculation gives the region where such phonon resonances may be expected, it is worthwhile to probe for these by suitable experimental means. Raman scattering and infrared absorption are potential experimental methods of detecting such resonances. Since no low-lying resonances are predicted and an appreciable number of vacancies would be present at high temperatures, thermal-conductivity studies at low temperatures are unlikely to show up the dips corresponding to these resonances, in contrast to the case of substitutional defects.

VI. CONCLUSIONS

A Green-function method has been applied to investigate phonon resonances due to a vacancy at the anion site in CaF_2, with the force-constant weakening estimated from detailed relaxation studies of the vacancy employing the potential of Catlow and Norgett and the HADES program. Symmetry coordinates have been employed to simplify the problem by block diagonalizing $\underline{g}$ and $\delta\underline{l}$. Phonon resonances are predicted around $x=0.66$ (310 cm^{-1}) for the A representation, around $x=0.76$ (380 cm^{-1}) for F_1 and around $x=0.36$ and 0.62 (170 cm^{-1}, 290 cm^{-1}) for the F_2 representation. Future experimental studies by Raman scattering and infrared absorption should be able to probe for these possible phonon resonances due to the anion vacancy in CaF_2 and hence throw more light on the role of the vacancy in disturbing the lattice and its normal modes.

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