RAMAN AND INFRA-RED STUDIES OF DEFECTS. _____

Theory of F-centre Raman scattering in SrF_2

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Résumé. — Les variations des forces et des constantes de force pour le centre F dans le SrF_2 ont été calculées en utilisant un modèle ion ponctuel, fonction d'onde du niveau fondamental. La variation négative prévue pour la constante de force centrale des plus proches cations est essentiellement en accord avec la valeur déduite des mesures des spectres Raman par Glynn, Hayes et Wiltshire. Une variation négative de la constante de force des plus proches anions est aussi prévue, contrairement à la grande valeur positive déduite des spectres. Toutefois, le déplacement radial dirigé vers l'extérieur, des plus proches cations peut produire une grande et positive variation de la constante de force centrale pour les troisièmes plus proches anions alignés avec les plus proches cations. Il apparaît maintenant que ce dernier effet fournit une meilleure explication pour une résonance A_1 observée dans le spectre de Raman à 310 cm^{-1} que l'hypothèse d'une variation positive de la constante de force pour les plus proches anions.

Abstract. — Forces and force-constant changes for the F centre in SrF_2 were calculated from a point-ion-model, ground-state wave function. The predicted negative central-force-constant change for NN cations is in essential agreement with the value inferred from measured Raman spectra by Glynn, Hayes and Wiltshire. The predicted force-constant change for NN anions is also negative, in contrast to the large positive value inferred from spectra. However, outward radial displacement of NN cations may produce a large, positive central force-constant change for those third-neighbor anions in line with NN cations. It now appears that the latter effect provides a better explanation for an observed A_1 resonance in the Raman spectrum at 310 cm^{-1} than does a hypothetical positive force-constant change for NN anions.

Glynn *et al.* [8] measured the single-phonon Raman spectra of F centres in SrF_2 , and interpreted the A_1 -symmetry spectrum in terms of the projections of the perturbed density of phonon states on symmetrical displacements of nearest cations and anions [4]. They exploited the large mass ratio of the ions by treating displacements of the cations and anions, which contribute to the Raman scattering in different frequency ranges, as independent; accordingly, they retained only two diagonal elements of the unperturbed Green's function matrix, calculated from a shell model of SrF_2 lattice dynamics [6]. The perturbation due to the defect was introduced by treating NN cation and anion central force constants as adjustable parameters [7]. The change of NN cation force constant required to give a good fit in the acoustic-mode frequency range was found to be $-9.9 e^2 V^{-1}$, where e is the electronic charge and V the volume of a primitive unit cell, a reduction of 60 %. An increase of effective NN anion force constant by between 18 and $45 e^2 V^{-1}$ was postulated to reproduce a resonance in the optic-mode frequency range at 310 cm^{-1} ,

where the density of unperturbed phonon states is very low [6]. The best fit to the measured spectrum was obtained with an increase of NN anion force constant by $20 e^2 V^{-1}$, but the predicted relative intensity associated with the resonance at 310 cm^{-1} is much greater than observed.

Point-ion wave functions for F centres in alkaline-earth fluorides were calculated by Bartram, Harmer and Hayes [1] for interpretation of ENDOR and Stark-effect data. We have employed their ground-state wave function for the F centre in SrF_2 in an *ab-initio* calculation of forces and force constants, with the object of explaining the empirical force-constant changes reported by Glynn *et al.* [8].

In the adiabatic approximation, forces and force constants are determined by the dependence of the ground-state energy on ion coordinates. Thus the force and diagonal force constant associated with ion displacement Q are given by

$$-\frac{\partial E_0}{\partial Q} = -\left\langle \psi_0 \left| \frac{\partial H}{\partial Q} \right| \psi_0 \right\rangle, \quad (1)$$

and

$$\frac{\partial^2 E_0}{\partial Q^2} = \left\langle \psi_0 \left| \frac{\partial^2 H}{\partial Q^2} \right| \psi_0 \right\rangle + 2 \left\langle \psi_0 \left| \frac{\partial H}{\partial Q} \right| \frac{\partial \psi_0}{\partial Q} \right\rangle, \quad (2)$$

where

$$H |\psi_n\rangle = E_n |\psi_n\rangle. \quad (3)$$

However, since the ground-state wave function was calculated by Bartram *et al.* [1] only for the perfect-lattice positions of ions, we expanded $|\partial\psi_0/\partial Q\rangle$ in the complete set of eigenfunctions $|\psi_n\rangle$ in order to transform the second term on the right-hand side of equation (2).

$$2 \left\langle \psi_0 \left| \frac{\partial H}{\partial Q} \right| \frac{\partial \psi_0}{\partial Q} \right\rangle = 2 \sum_{n>0} \frac{|\langle \psi_n | \partial H / \partial Q | \psi_0 \rangle|^2}{E_0 - E_n}. \quad (4)$$

Finally, we employed the closure approximation to obtain

$$\begin{aligned} \frac{\partial^2 E_0}{\partial Q^2} &\approx \left\langle \psi_0 \left| \frac{\partial^2 H}{\partial Q^2} \right| \psi_0 \right\rangle - \frac{2}{\Delta E} \times \\ &\times \left\{ \left\langle \psi_0 \left| \left(\frac{\partial H}{\partial Q} \right)^2 \right| \psi_0 \right\rangle - \left(\frac{\partial E_0}{\partial Q} \right)^2 \right\}. \end{aligned} \quad (5)$$

The greatest uncertainty in the present calculation arises from the choice of an appropriate energy denominator ΔE in equation (5). Accordingly, we have extended the calculations of Bartram *et al.* [1] to incorporate symmetrical displacements of the NN cations, and have evaluated the corresponding force-constant change by numerical differentiation. The value $\Delta E = 0.948$ Ry, chosen to insure agreement of the approximate force constant change from equation (5) with that determined numerically for NN cations, was employed for the anions as well.

The required derivatives of the point-ion potential for A_1 displacements, expanded in spherical harmonics about the anion vacancy, are

$$\begin{aligned} \frac{\partial V_{\text{PI}}(r)}{\partial r_s} &= - \sum_{L=0}^{\infty} \sum_{M=-L}^L Y_L^M(\theta, \varphi) \times \\ &\times \left\{ \begin{aligned} &-(L+1) f_{LMs} r^L / r_s^{L+2}, r < r_s \\ &L f_{LMs} r_s^{L-1} / r^{L+1}, r > r_s \end{aligned} \right\} \end{aligned} \quad (6)$$

and

$$\begin{aligned} \frac{\partial^2 V_{\text{PI}}(r)}{\partial r_s^2} &= - \sum_{L=0}^{\infty} \sum_{M=-L}^L Y_L^M(\theta, \varphi) \times \\ &\times \left\{ \begin{aligned} &(L+1)(L+2) f_{LMs} r^L / r_s^{L+3}, r < r_s \\ &L(L-1) f_{LMs} r_s^{L-2} / r^{L+1}, r > r_s \end{aligned} \right\} \end{aligned} \quad (7)$$

where

$$f_{LMs} \equiv \sum_{\alpha} \frac{8\pi Q_{\alpha}}{2L+1} Y_L^{M*}(\theta_{\alpha}, \varphi_{\alpha}), \quad (8)$$

$(r_{\alpha} = r_s)$

Here, Q_{α} is the charge on ion α whose polar coordinates with respect to the vacancy centre are r_{α} , θ_{α} and φ_{α} ; r_s is the radius of ion shell s ; and $Y_L^M(\theta, \varphi)$ is a spherical harmonic. Energies are in Rydbergs and displacements in Bohr radii.

The approximate ground-state wave function, determined variationally, is of the form [1]

$$\begin{aligned} \psi_0(\mathbf{r}) &= (1 - C^2)^{1/2} (\alpha^3/7\pi)^{1/2} (1 + \alpha r) \exp(-\alpha r) + \\ &+ C(\beta^9/3\pi)^{1/2} (xyz) \exp(-\beta r), \end{aligned} \quad (9)$$

where $\alpha = 0.56$, $\beta = 0.89$ and $C = -0.506$.

Since ψ_0 is restricted to a combination of s- and f-orbitals, the only terms in equations (6) and (7) which contribute to matrix elements of $\partial V_{\text{PI}}/\partial r_s$ and $\partial^2 V_{\text{PI}}/\partial r_s^2$ are those with $L = 0, M = 0$; $L = 3, M = \pm 2$; $L = 4, M = 0, \pm 4$; and $L = 6, M = 0, \pm 4$. In principle, an infinite set of terms contributes to matrix elements of $(\partial V_{\text{PI}}/\partial r_s)^2$; however, terms with higher L values correspond to intermediate states of high angular momentum in equation (4). Since inclusion of high-angular-momentum states in the expansion of $|\partial\psi_0/\partial Q\rangle$ is incompatible with the smooth variational trial function of equation (9), we have omitted terms with $L, L' > 3$ in the expression of $(\partial V_{\text{PI}}/\partial r_s)^2$.

We have calculated the forces and force-constant changes associated with symmetrical displacements of three shells of ions as shown in figures 1: (1) nearest-

Fig. 1. — Radial displacements of ions in lattice relaxation about SrF_2 F centre. Numbers designate shells of ions referred to in text.

neighbor cations, (2) next-nearest neighbor anions, and (3) anions just beyond and in line with the nearest-neighbor cations. For convenience, we have introduced symmetry-adapted coordinates defined by $Q_s \equiv (n_s)^{1/2} r_s$, where n_s is the number of ions on shell s . The corresponding forces, calculated from equations (1), (6) and (9), are listed in table I, and the force constants, calculated from equations (5), (7) and (9), are listed in table II.

Additional contributions to both forces and force-constant changes arise from deletion of the Coulomb and short-range repulsive interactions of the missing

anion. Derivatives of the short-range repulsive interaction were calculated from the Born-Mayer (Pauling) potentials of Benson and Dempsey [5]. These additional contributions are also listed in tables I and II. Contributions to forces and force-constant changes from finite-ion-size effects [2] are not included in the present calculation.

Table I. — Contributions to forces on shells of ions in units of $ae^2 V^{-1}$, where a is the edge length of a conventional fcc unit cell, and $V (= a^3/4)$ is the volume of a primitive unit cell. Shells are numbered in accordance with figure 1.

	Shell		
	1	2	3
$-\partial E_0/\partial Q_s$	- 3.063 7	+ 1.836 0	+ 0.594 1
$-\partial E_{\text{coul}}/\partial Q_s$	+ 5.333 4	- 2.449 5	- 0.666 7
$-\partial E_{\text{rep}}/\partial Q_s$	- 1.151 2	- 0.320 5	—
F_{total}	+ 1.118 5	- 0.934	- 0.072 6

Table II. — Contributions to force-constant changes in units of $e^2 V^{-1}$.

	Shell		
	1	2	3
$\partial^2 E_0/\partial Q_s^2$	- 13.276 0	+ 0.638 8	+ 0.589 7
$\partial^2 E_{\text{coul}}/\partial Q_s^2$	+ 12.316 8	- 4.000 0	- 0.769 8
$\partial^2 E_{\text{rep}}/\partial Q_s^2$	- 10.113 4	- 4.874 4	0
Total (theory)	- 11.072 6	- 8.235 6	- 0.180 1
Experiment	- 9.9	+ 20	

The total forces listed in table I act on the ions in their perfect lattice positions to produce lattice distortions. Radial displacements of the ions corresponding to these forces are shown schematically in figure 1. The real parts of the lattice Green's functions at zero frequency were used to determine the response of shells 1 and 2 to the applied forces.

It is evident from table II that the calculated total central force-constant change for NN cations (shell 1) agrees very well with the value inferred from Raman spectra [8]. The force constant change associated with this shell accounts very well for the Raman scattering observed in the acoustic mode region [8]. On the other hand, the calculated central force-constant change for NN anions (shell 2) is completely at variance with the reported experimental value. The calculated change is negative, and in fact no mechanism is apparent for a positive change since the relative displacement of NN cations and anions is such as to increase their separation. Other shells of ions are less directly affected by the F centre, but an indirect effect of the large outward displacements of NN cations is a substantial increase in the central force constant for third neighbor (shell-3) anions. An analogous effect has been reported for the F centre in KCl [3]. The foregoing results lead us to re-interpret the measured Raman spectra in the optic mode region. It now seems apparent that the central-force-constant change for shell 3 anions is responsible for the resonance at 310 cm^{-1} , and that the relatively low intensity associated with this resonance is a consequence of relatively weak coupling of the electronic system to displacements of shell-3 anions [4]. The negative force-constant change for shell-2 anions will contribute to the spectrum in the optic-mode region, although not to the resonance.

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