Quadratic electron–lattice interaction and vacancy effect in the divalent Sn^{2+} ion centre in alkali halide crystals: a theoretical calculation

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Abstract. Absorption and magnetic circular dichroism (MCD) spectra of band C for the Sn^{2+} centre in alkali halide crystals have been calculated by means of the Monte Carlo integration method. The calculated spectra are compared with the asymmetric absorption and inversion-asymmetric MCD spectra observed in $KCl:Sn^{2+}$ crystals. A good fit to the observation is obtained taking into account both the quadratic electron–lattice interaction with the T_{2g} vibrational mode and the charge-compensating vacancy in addition to the linear electron–lattice interaction. It is shown that, although the quadratic interaction gives rise to an asymmetric MCD lineshape, the vacancy is important to derive the spectra which agree with the observations for both the absorption and the MCD.

1. Introduction

The dynamical Jahn–Teller effect is strong in impurity ions with the s^2 outer-electron configuration (e.g. In^+, Tl^+, Ga^+, Sn^{2+} and Pb^{2+}) which are incorporated substitutionally in alkali halide crystals (see, e.g. Tsuboi (1981), Ranfagni et al (1983) and Jacobs (1991)). The effect is clearly observed in the lineshapes of the absorption bands A, B and C, especially in the symmetric triplet structure of band C observed for In^+ centres (Fukuda 1964). In addition to the linear electron–lattice interaction, a quadratic electron–lattice interaction has been introduced to explain the asymmetric triplet structure of band C which is observed for Tl^+ and Sn^{2+} centres (see, e.g. Honma (1969), Uchida and Tsuboi (1968) and Tsuboi et al (1973)). The magnetic circular dichroism (MCD) spectra are known to give important information on the electronic states of the localized centres and their electron–lattice interactions. Recently we confirmed the importance of the quadratic interaction from the MCD spectra of band C observed for $KCl:Sn^{2+}$ and $RbCl:Sn^{2+}$ crystals (Tsuboi and Hori 1992). The observed band C MCD spectrum of $KCl:Sn^{2+}$ is shown in figure 1, together with the absorption spectrum. Unlike the cases of monovalent In^+, Tl^+ and Ga^+ ion centres where the inversion-symmetric MCD spectra have been observed (Grasso et al 1972, 1973, Bagnato et al 1975, Le Si Dang et al 1978, Kamishina et al 1979), the inversion-asymmetric band C MCD spectra have been observed not only for $KCl:Sn^{2+}$ and $RbCl:Sn^{2+}$ (Tsuboi and Hori 1992) but also for $KBr:Sn^{2+}$ (Scacco et al 1982).

Such asymmetric band C MCD lineshapes were observed for $KI:Sn^{2+}$, $KBr:Sn^{2+}$ and $KCl:Sn^{2+}$ in 1981 by the first author of the present paper when he was measuring the MCD spectra of bands A and B for various s^2 ion centres (Tsuboi 1981). He hesitated to report
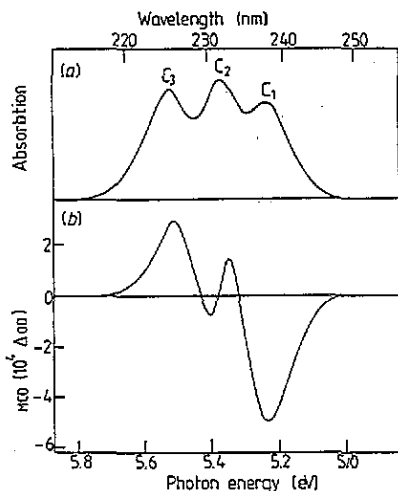
Figure 1. (*a*) The absorption and (*b*) the MCD spectra of band C for $KCl:Sn^{2+}$ measured at 22 K. The applied magnetic field is 11.5 kG. Δ OD means $OD_L - OD_R$, where OD_L and OD_R represent the optical densities measured using left- and right-handed circularly polarized light components, respectively. The background (including the overlapping of band B) is subtracted in both the spectra.

the spectra at that time because the lineshapes were quite different from those that had been observed for Tl^+ and In^+ centres and because it was not confirmed definitely that there is no problem in the background subtraction in the spectral region. In fact, Scacco *et al* (1982) suggested the possibility that the unusual band C MCD spectrum observed for $KBr:Sn^{2+}$ might arise from the uncertainty in the background subtraction. Now, from observations for various Sn^{2+}-doped crystals and from measurements using lightly doped crystals with less than 0.005 mol% Sn^{2+} and thin crystals with a thickness of about 0.5 mm to avoid the background problem, we have confirmed that these spectra are not artefacts but true spectra.

In our recent paper, we tried to calculate the MCD lineshape taking into account a quadratic electron–lattice interaction with the T_{2g} vibrational mode using several values of coupling constants for the lattice vibrations (Tsuboi and Hori 1992). The inversion-asymmetric lineshape was obtained by the quadratic interaction, but the calculated MCD is not exactly in agreement with the obsreved spectrum. In the present investigation, we undertake the calculations of both the absorption and the MCD spectra to explain the observed spectra quite well. Unlike monovalent ions such as Tl^+, it is probable that the divalent Sn^{2+} ion is accompanied by a charge-compensating cation vacancy at its near position in alkali halide crystals. Here we take into account the vacancy effect in addition to the linear and quadratic electron–lattice interactions.

2. Methods of calculation

The Sn^{2+} ion in a cubic crystal field has an $(a_{1g})^2$ electron configuration in the ground state and an $(a_{1g})(t_{1u})$ configuration in the first excited state. The former configuration leads to formation of the $^1A_{1g}$ ground state, while the latter to the five states $^1A_{1u}$, $^3T_{1u}$, ^3E_u, $^3T_{2u}$ and $^1T_{1u}$. The Coulomb and spin–orbit interactions lead to mixing of these states. As a

result, the excited state of band C (called state C) is described by

$$|C_j\rangle = [R/(R+1)]^{1/2}|{}^1T_{1u,j}\rangle + [1/(R+1)]^{1/2}|{}^3T_{1u,j}\rangle \qquad (j = x, y, z)$$

where R is the intensity ratio of the dipole strength of band C to that of band A (Honma 1968, Farge and Fontana 1979).

The electron–lattice interaction Hamiltonian H_{eL} for state C has been given by Toyozawa and Inoue (1966) as follows:

$$H_{eL} = c_1 \mathbf{T} Q + (a_1' \mathbf{1} + b_1' \mathbf{T}^2) Q^2 \tag{1}$$

where

$$c_1 = (R - \tfrac{1}{2})c/(R+1)$$

$$a_1' = c^2/(R+1)E_{CB}$$

$$b_1' = -3c^2/4(R+1)E_{CB} + 9Rc^2/(R+1)^2 E_{CA} \tag{2}$$

$$Q = (Q_4^2 + Q_5^2 + Q_6^2)^{1/2}$$

$$\mathbf{T} = \begin{bmatrix} 0 & n & m \\ n & 0 & l \\ m & l & 0 \end{bmatrix}$$

l, m and n are the direction cosines of Q_4, Q_5 and Q_6, respectively, and $\mathbf{1}$ is the unit matrix. $E_{CA}(= E_C - E_A)$ means the energy separation of bands C and A, and c is the coupling constant for the T_{2g} vibrational mode. The linear term in equation (1) is constructed using the basis functions $|x\rangle$, $|y\rangle$ and $|z\rangle$ (more exactly, the basis functions $|C_x\rangle$, $|C_y\rangle$ and $|C_z\rangle$). The quadratic terms in equation (1) are the second-order perturbation which comes from the mixing of state C with states A and B. In the above Hamiltonian, only the T_{2g} mode (Q_4, Q_5 and Q_6) is taken into account because this mode is responsible for the triplet structure of band C. For KCl:Sn^{2+} with values of $R = 18$, $E_{CB} = 0.54$ eV and $E_{CA} = 1.02$ eV, the coupling constant a_1' is larger than the coupling constant b_1', i.e. $a_1'/b_1' = 4.515$. Therefore we neglect the second term of the quadratic terms in equation (1). The same holds for the other Sn^{2+}-doped alkali halides. According to Honma (1969), unlike the quadratic interaction with the T_{2g} mode, the quadratic terms due to the A_{1g} and E_g modes, i.e. Q_1^2 and $Q_2^2 + Q_3^2$, do not give an appreciable effect to induce asymmetry in the band-C lineshape. Therefore we neglect the quadratic electron–lattice interaction with the A_{1g} and E_g modes hereafter.

The divalent Sn^{2+} ion has a charge-compensating cation vacancy near the impurity ions in alkali halide crystals. Two types are conceivable as the position of the vacancy: one occupies a nearest-neighbour cation lattice, and the other occupies a next-nearest-neighbour cation lattice. The former leads to the rhombic Sn^{2+} centre, while the latter to the tetragonal centre. Since the ionic radius of Sn^{2+} (0.93 Å) is smaller than that of K^+ (1.33 Å), the Sn^{2+} centre is expected to be a tetragonal centre (Scacco and Jacobs 1982). Therefore we assume that the Sn^{2+} ions have a tetragonal crystal field in alkali halides.

The interaction matrix H' for state C, which consists of the linear electron–lattice interaction with A_{1g} (Q_1), E_g (Q_2 and Q_3) and T_{2g} (Q_4, Q_5 and Q_6) modes (Cho 1969),

the tetragonal crystal field, the Zeeman energy and the quadratic electron–lattice interaction with the T_{2g} mode, is given by

$$
H' = aQ_1 \mathbf{1} +
\begin{array}{ccc}
|+\rangle & |0\rangle & |-\rangle
\end{array}
$$

$$
H' = aQ_1 \mathbf{1} +
\begin{pmatrix}
gH - (b/\sqrt{3})Q_3 - D & (c/\sqrt{2})(Q_5 - iQ_4) & bQ_2 - icQ_6 \\
(c/\sqrt{2})(Q_5 + iQ_4) & (2/\sqrt{3})bQ_3 + 2D & (c/\sqrt{2})(Q_5 - iQ_4) \\
bQ_2 + icQ_6 & (c/\sqrt{2})(Q_5 + iQ_4) & -gH - (b/\sqrt{3})Q_3 - D
\end{pmatrix}
$$

$$
+ a_1'(Q_4^2 + Q_5^2 + Q_6^2)\mathbf{1} \tag{3}
$$

where $a_1 = (R - \frac{1}{2})a/(R + 1)$ and $b_1 = (R - \frac{1}{2})b/(R + 1)$, and a and b are the coupling constants for the A_{1g} and E_g vibrational modes, respectively. The basis functions in the Hamiltonian in equation (3) are

$$
|+\rangle = \tfrac{1}{2}(|x\rangle + i|y\rangle)
$$
$$
|-\rangle = \tfrac{1}{2}(|x\rangle - i|y\rangle)
$$
$$
|0\rangle = |z\rangle
$$

($|x\rangle$ means $|C_x\rangle$ as mentioned above), gH is the Zeeman energy in the case when a magnetic field H is applied to the z axis, and D is a parameter which reflects the strength of the tetragonal field (due to the vacancy) of the Sn^{2+} ion.

In the classical Franck–Condon approximation, the lineshape function of the optical absorption is given by

$$
F(E) = \frac{1}{(\pi kT)^3} \int \cdots \int dQ_1 \ldots dQ_6 \exp\left(\frac{-1}{kT}(Q_1^2 + \ldots + Q_6^2)\right) \frac{1}{3} \sum_{l=1}^{3} \delta[E - E_C - X_l(Q)]
$$
$$
\tag{4}
$$

$$
Q^2 = (Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2 + Q_5^2 + Q_6^2)
$$

for band C which is due to the electronic transition from the ground state $|s\rangle$ to state C ($|+\rangle, |0\rangle, |-\rangle$), where $X_l(Q_1, Q_2, Q_3, Q_4, Q_5, Q_6)$ is the eigenvalue of H' when $H = 0$, and E is the photon energy (Cho 1969). On the other hand, the lineshape function for MCD is given by

$$
f(E) = f_+(E) - f_-(E) = \frac{1}{(\pi kT)^3} \int \cdots \int dQ_1 \ldots dQ_6 \exp(-Q^2/kT)
$$

$$
\times \frac{1}{3} \sum_{l=1}^{3} \delta[E - E_c - X_l(Q)]\{|\langle 0|M_+|l\rangle|^2 - |\langle 0|M_-|l\rangle|^2\} \tag{5}
$$

where M_+ and M_- are the electric dipole moment operators in the circular polarization, i.e. $M_+ = x + iy$ and $M_- = x - iy$, $|l\rangle$ ($l = 1, 2, 3$) is the eigenvector of H', and E_C is the excitation energy of band C at $(Q_1, Q_2, Q_3, Q_4, Q_5, Q_6) = 0$ (Cho 1969).

We calculate the function $F(E)$ under zero magnetic field and the function $f(E)$ by means of the Monte Carlo integration method to evaluate the integral over six coordinates Q_1 to Q_6, as was done by Cho (1969). The numerical calculation is carried out in terms of 100 000 sets of six random numbers Q_1, Q_2, Q_3, Q_4, Q_5 and Q_6. These calculations are made using the SVR4 computer system (NEC EWS 4800RISC system) at the Kyoto Institute of Technology.

3. Calculation results and discussion

We have calculated the functions $F(E)$ and $f(E)$ using various combinations of the values of D, a_1, b_1, c_1 and a_1'. The $F(E)$ lineshape is slightly changed by increasing the tetragonal field parameter D if the ratio $a_1 : b_1 : c_1$ and the a_1'-value are fixed. However, the MCD lineshape (i.e. function $f(E)$) is changed by varying the D-value. The amount of the positive MCD peak appearing on the high-energy side (denoted MCD$_+$) becomes smaller than the amount of the negative MCD appearing on the low-energy side (MCD$_-$); for example, the ratios M ($=$ MCD$_+$/MCD$_-$) are 0.92, 0.92, 0.88 and 0.62 for $D = 0.0, 0.001, 0.01$ and 0.1, respectively, in the case when $a_1 : b_1 : c_1 = 0.0 : 0.3 : 0.7$ and $a_1' = 0.13$. No appreciable tetragonal field effect is observed when D is as small as 0.001. When the D-value is not changed and the a_1'-value is also not changed, the asymmetry in the $F(E)$ lineshape is enhanced by increasing the ratio $b_1 : c_1$ but the asymmetry in the $f(E)$ lineshape is reduced. On the other hand, as the a_1'-value is increased in the case when the ratio $a_1 : b_1 : c_1$ and the D-value are fixed, the $f(E)$ lineshape is slightly changed but the peak height ratio P of component C_3 to component C_1 (see figure 1) becomes large, i.e. the $F(E)$ lineshape becomes more asymmetric.

On increasing the value of D but without changing the values of a_1, b_1, c_1 and a_1', the C_2–C_3 separation is observed to become larger than the C_1–C_2 separation in the $F(E)$ function and component C_3 is observed to decrease more rapidly than component C_1; as a result the peak of C_3 becomes lower than that of C_1 in the case of a large value such as $D = 0.5$. The reversal of the peak height between components C_1 and C_3 disagrees with the experimental result. Moreover the $f(E)$ function in such a case is in disagreement with the observed MCD spectra.
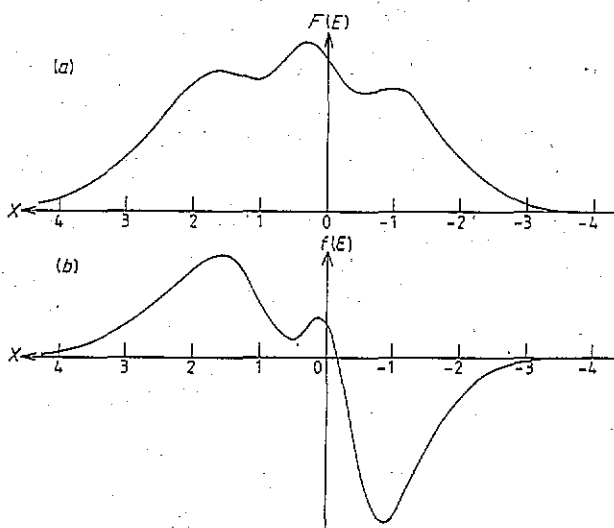

Figure 2. (a) The absorption $F(E)$ and (b) the MCD $f(E)$ functions which are calculated using values of $a_1 : b_1 : c_1 = 0 : 0.3 : 0.7$, $a_1' = 0.2$ and $D = 0.1$. For the abscissae, $X = (E - E_C)/[kT(2b^2/3 + c^2)]^{1/2}$, where E is the photon energy.

Figure 2 shows an $F(E)$ function and its corresponding $f(E)$ function which are obtained by choosing the values of $a_1 : b_1 : c_1 = 0.0 : 0.3 : 0.7$, $a_1' = 0.2$ and $D = 0.1$.

The $F(E)$ and $f(E)$ lineshapes, which give the ratios $P = 1.12$ and $M = 0.62$, are similar to the observed absorption and MCD spectra in figure 1.

From the calculations of the $F(E)$ and $f(E)$ functions we have found that the asymmetric triplet structure of the absorption spectrum and the inversion-asymmetric MCD spectrum observed in band C for KCl:Sn^{2+} and RbCl:Sn^{2+} are explained satisfactorily by taking into account the linear electron–lattice interaction, the quadratic interaction and the tetragonal crystal-field interaction by the charge-compensating vacancy. Although the last two interactions give rise to asymmetry in both the absorption and the MCD lineshapes, the vacancy effect cannot be neglected to obtain the $F(E)$ and $f(E)$ functions which are in agreement with experiment. Scacco and Jacobs (1982) suggested from their calculation of the absorption lineshape for KBr:Sn^{2+} that 75% of the divalent Sn^{2+} ions distributed in monovalent KBr lattice positions are not accompanied by the vacancy and the other 25% are accompanied by the vacancy. It is difficult to understand the reasons why some Sn^{2+} ions are accompanied by a vacancy and some are not and why such a relatively small number of Sn^{2+} ions have a vacancy while the majority of Sn^{2+} ions do not. We suggest and believe that there is no difference between the Sn^{2+} ions entering into the crystal. The result of the present calculation supports this suggestion.

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