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Quadratic electron–lattice interaction in the Sn^{2+}-ion centre in alkali halide crystals

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Abstract. Magnetic circular dichroism (MCD) spectra of the C band of KCl:Sn^{2+} and RbCl:Sn^{2+} crystals have been investigated experimentally. Coupling to the T_{2g} vibrational mode is confirmed to be present in the C band of the Sn^{2+} centre. The observed inversion-asymmetric MCD lineshape is understood in terms of a quadratic electron–lattice interaction.

1. Introduction

Electron–lattice interaction plays an essential role in the optical absorption spectra of defect centres in solids. The Jahn–Teller effect, i.e. a linear electron–lattice interaction, has been observed to give rise to a splitting or structure in the absorption bands. In addition to the linear electron–lattice interaction, a quadratic electron–lattice interaction is also conceivable as an element to determine the lineshape of the absorption band. A considerable number of papers have been published on the Jahn–Teller-effect-induced band splitting (Bersuker 1984), but there are few papers concerning the quadratic-interaction-involved absorption bands. The present paper was undertaken to find the contribution of the quadratic interaction in defect centres using a magnetic circular dichroism (MCD) measurement of s^2-ion centres.

Tl^+, In^+, Ga^+, Sn^{2+}, Pb^{2+}, Au^-, Ag^- and Cu^- ions are classified as s^2 ions since they have an s^2 electron configuration outside a closed shell in the ground state. Alkali halide crystals containing these ions exhibit three optical absorption bands denoted A, B and C in order of increasing energy (Lushchik and Zazubovich 1972, Hizhnyakov and Kristoffel 1984). These bands arise from the $s^2 \rightarrow sp$ electronic transition of the s^2 ion. A doublet structure and a triplet structure have been observed for the A and C bands (Tsuboi *et al* 1973, 1975, Tsuboi 1981). The observed structure is caused by the Jahn–Teller interaction of the s and p electrons with the T_{2g} lattice vibrations (Toyozawa and Inoue 1966, Cho 1968, Hizhnyakov and Kristoffel 1984). According to theoretical calculations made using a linear electron–lattice interaction (Honma and Ooaku 1966, Toyozawa and Inoue 1966, Cho 1968), firstly, electron coupling to the A_{1g} or E_g vibrational mode gives rise to a structureless C band, secondly, coupling to the T_{2g} mode yields a triplet structure with a very sharp peak at the centre of the band and, thirdly, coupling to two of T_{2g} and E_g modes, or of the T_{2g} and A_{1g} modes,

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gives a triplet structure as shown in figure 1. The theoretical MCD lineshape has been derived (Honma and Ooaku 1966, Cho 1969) which is also shown in figure 1. In the A_{1g}- or E_g-mode coupling, an absorption-derivative MCD lineshape is produced (figure 1(*a*)) while, in the T_{2g}-mode coupling, an additional S-shaped curve appears in the central part of the C band (figure 1(*b*)) but the intensity of the central structure becomes relatively small when the A_{1g} or E_g mode is coupled (figure 1(*c*)).

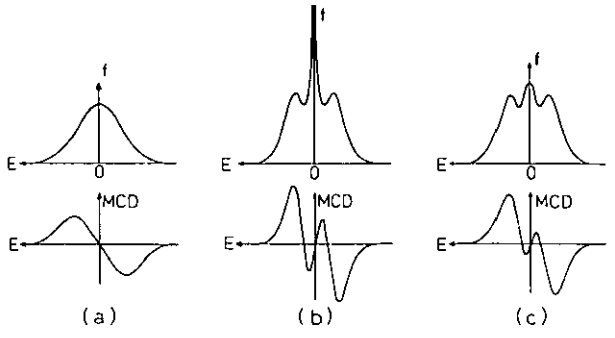

Figure 1. Schematic absorption and MCD lineshape of the C band for (*a*) A_{1g}- or E_g-vibration-mode coupling, (*b*) T_{2g}-mode coupling and (*c*) coupling of T_{2g} and A_{1g} modes or coupling of T_{2g} and E_g modes. E is the photon energy relative to the centre of the C band; the MCD equals $OD_L - OD_R$.

The C band, which is due to the $^1A_{1g} \rightarrow {}^1T_{1u}$ electronic transition, has a triplet-structured lineshape for the Sn^{2+}, In^+ and Tl^+ centres (Ranfagni *et al* 1983). Of the three centres, a well resolved structure is observed for the Sn^{2+} centres, indicating a strong T_{2g}-mode coupling. In the present paper we try to determine whether the MCD lineshape can reveal the contribution from the linear and quadratic interactions with the T_{2g} mode. Here we investigate the C band of KCl:Sn^{2+} and RbCl:Sn^{2+} crystals.

2. Experimental procedure

Single crystals of KCl and RbCl containing $SnCl_2$ were grown by the Stockbarger method. The concentrations of $SnCl_2$ were chosen to be less than 0.005 mol% in the melt. In order to produce the isolated Sn^{2+} centre and to avoid the Sn^{2+} aggregate centre, the crystals were heated at 450 °C for 25 min and rapidly quenched to room temperature on a copper plate, immediately before the absorption and MCD measurements.

The MCD and absorption were measured using a JASCO J-40A spectropolarimeter. The absorption spectra were also measured using a Shimadzu UV-260 spectrophotometer. The MCD is given by the difference between the optical densities (OD), $OD_L - OD_R$, for the left and right circularly polarized components of light. The polarized light propagates through a crystal parallel to a magnetic field, along the [001] direction. A JASCO electromagnet was used to produce the field. The MCD lineshape was obtained by subtracting the background which was a CD signal measured at zero field.

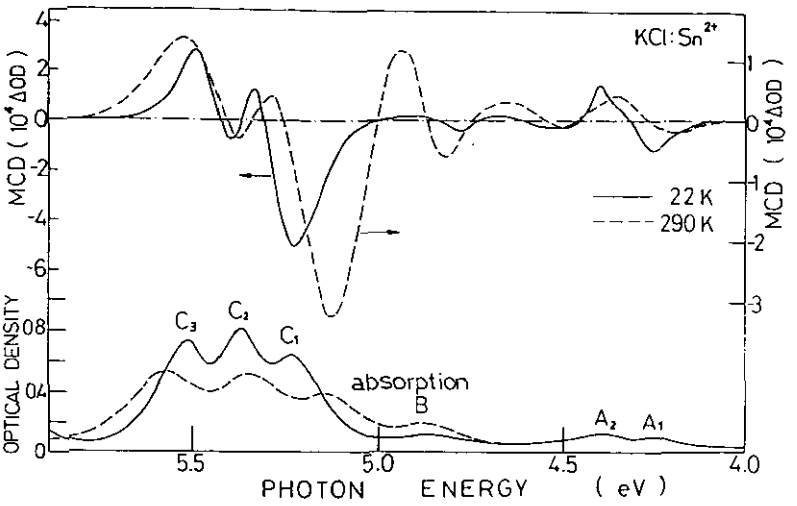

Figure 2. The MCD (upper part) and absorption (lower part) spectra of a KCl:Sn^{2+} crystal at 290 K (– – –, scale on right) and at 22 K (——, scale on left). The applied magnetic field is 11.5 kG. ΔOD means $OD_L - OD_R$.

3. Experimental results and discussion

Figure 2 shows the MCD spectra of the A, B and C bands for KCl:Sn^{2+} at room temperature (290 K) and at 22 K, together with the absorption spectra. It is observed that a negative MCD peak appears near the C_1-band peak and a positive peak appears near the C_3-band peak, and a weak S-shaped curve appears around the C_2-band peak. Thus, the C_1, C_2 and C_3 components of the C band give rise to the negative, S-shaped and positive MCD signals, respectively. A quite similar MCD lineshape is also observed for the triplet-structured C band of RbCl:Sn^{2+}, as shown in figure 3. When the temperature is decreased, the MCD signal of the C band becomes intense and narrow but no large change is observed in the shape. The observed MCD spectra of the A and B bands agree with the previous results (Fukuda *et al* 1976, Tsuboi 1981, Scacco *et al* 1982).

The C-band MCD lineshape of KCl:Sn^{2+} and RbCl:Sn^{2+} is similar to the lineshape shown in figure 1(*c*), which was calculated using $a : b : c = 0.4 : 1.0 : 1.0$, where a, b and c are the coupling strengths with the A_{1g}, E_g and T_{2g} modes, respectively (Cho 1969). Therefore it is confirmed that the T_{2g} mode contributes to determining the lineshape of the C band. When we compare the C-band MCD lineshape observed for KCl:Sn^{2+} and RbCl:Sn^{2+} with the theoretical lineshape in detail, we find a difference between the two. Unlike the lineshape in figure 1(*c*), which was obtained using a linear electron–lattice interaction, the observed MCD lineshape is not inversion symmetric; the amount of the positive peak appearing around the C_3 band is not the same as that of the negative peak appearing around the C_1 band, but the former is smaller than the latter.

As seen in the lower parts of figures 2 and 3, the C band has an asymmetric triplet structure where the C_3 band is higher than the C_1 band. Such an asymmetry is caused by the quadratic electron–lattice interaction with the T_{2g} vibrational mode, which results from a difference between the curvatures of the $^1T_{1u}$ and $^1A_{1g}$ energy

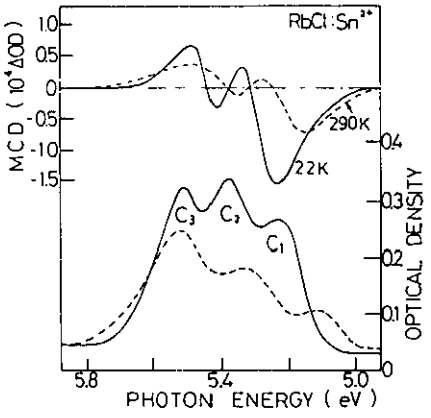

Figure 3. The MCD and absorption spectra for the C band of an RbCl:Sn^{2+} crystal at 290 K and 22 K. The applied magnetic field is 12.4 kG. ΔOD means $OD_L - OD_R$.

surfaces (Honma 1968, 1969). Therefore, the observed asymmetric MCD lineshape is suggested to be caused by the quadratic interaction of the T_{2g} mode. Unlike the case of the Sn^{2+} centre, the In^+ and Tl^+ centres, where the quadratic interaction is not strong, have a symmetric triplet structure for the C band (Fukuda 1964, Jacobs and Oyama 1975) and therefore an inversion-symmetric MCD lineshape (Bagnato *et al* 1975, Grasso *et al* 1972, 1973) which is similar to the curve in figure 1(*b*). A similar inversion-asymmetric MCD lineshape was also observed for the C band of a KBr:Sn^{2+} crystal (Scacco *et al* 1982). It is noted that the C band of KBr:Sn^{2+} has the same asymmetric triplet structure as those of KCl:Sn^{2+} and RbCl:Sn^{2+}. According to the result of calculations made using a Monte Carlo method, an inversion-asymmetric MCD lineshape is obtained by taking into account the quadratic interaction with the T_{2g} mode, as shown in figure 4. Figure 4 shows the MCD lineshapes, calculated using the same Monte Carlo method as employed by Cho (1968, 1969), in the cases $\gamma = 0$ and $\gamma = -0.13$, where γ is the quadratic electron–lattice interaction coupling constant for the T_{2g} mode as used by Honma (1969). It is observed that, as the quadratic interaction is added to the linear interaction, the centre of the inversion-symmetric MCD lineshape is shifted towards a high energy and deviates from the zero MCD value, giving rise to an asymmetric lineshape. As a result, it is suggested that the quadratic electron–lattice interaction is responsible for the formation of the inversion-asymmetric C-band MCD lineshape of KCl:Sn^{2+} and RbCl:Sn^{2+}.

As an alternative explanation for the asymmetric C-band MCD lineshape, one may propose an influence of the D band which is located near the C band (Scacco *et al* 1982). The D band, however, is not supposed to give such a lineshape. The reason is as follows. The separation between the C and D bands is smaller for In^+ and Tl^+ centres than for Sn^{2+} centres; for example, the separations between the central component (C_2) of the C band and the lowest component (D_1) of the D band are 1.33 eV and 0.38 eV for KCl:In^+ and KCl:Tl^+, respectively, and 1.42 eV for KCl:Sn^{2+} (Ranfagni *et al* 1983). The effect of the D band on the C band is expected to be stronger for In^+ and Tl^+ centres than for Sn^{2+} centres since it depends on the amount of the band separation, but a symmetric MCD lineshape has been observed for the former centres.

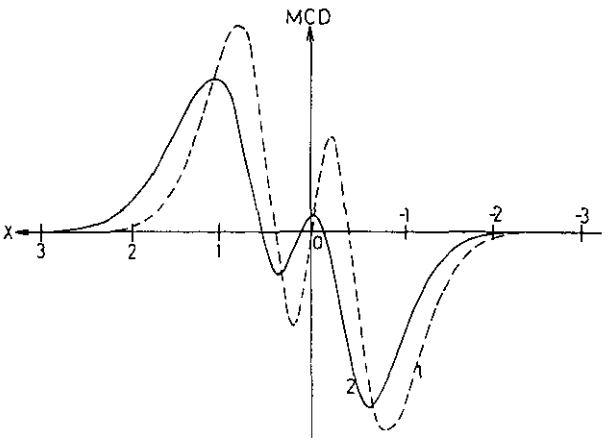

Figure 4. The MCD lineshapes calculated using $a : b : c = 0.0 : 0.5 : 0.5$ and $\gamma = 0$ (curve 1) and $\gamma = -0.13$ (curve 2), where a, b and c are the linear electron–lattice coupling constants for the A_{1g}, E_g and T_{2g} modes, respectively, and γ is the quadratic coupling constant for the T_{2g} mode, obtained by means of the same Monte Carlo method as employed by Cho (1968, 1969). The numerical calculation was carried out in terms of 10 000 sets of six random numbers Q_1, Q_2, Q_3, Q_4, Q_5 and Q_6. In the abscissa, x means $E/[kT(\frac{2}{3}b^2 + c^2)]^{1/2}$, where E is the energy.

In conclusion, it is suggested from the observed MCD spectra that the C band of Sn^{2+} centres is caused not only by the Jahn–Teller-active T_{2g} mode but also by the quadratic interaction with the T_{2g} mode.

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