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Optical absorption of the off-centred Ge^{2+} ions in KCl and KBr crystals

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Received 10 May 1994

Abstract. Optical absorption spectra of Ge^{2+} ions in KCl and KBr crystals have been investigated in the temperature range 15–300 K. In the triplet-structured spin-orbit-allowed C band, the C_1 – C_2 band splitting was observed to be larger than that of the C_2 – C_3 band at low temperatures, while the two become equal to each other with increasing temperature. The absorption lineshape has been calculated, by means of the Monte Carlo integration method, for Ge^{2+} ions with a linear electron–lattice interaction and tetragonal crystal field. Comparing the calculated lineshape with the observed spectra, we conclude that the Ge^{2+} ion is at the off-centre position with the tetragonal field at low temperatures, but is moved into the on-centre position with increasing temperature.

1. Introduction

Impurity ions which are doped in alkali-halide crystals give rise to optical absorption in a transparent region of the bulk crystal. The analyses of the absorption spectra provide valuable information on the electronic states and geometrical structure of the impurity ions. Alkali-halide crystals containing a small amount of Tl^+ -like ions with s^2 ground-state electron configuration exhibit three absorption bands due to the $(a_{1g})^2 \rightarrow (a_{1g})(t_{1u})$ electronic transition in the s^2 ion centres (Ranfagni *et al* 1983, Henderson and Imbusch 1989). They have been called A, B and C bands in order of increasing energy. The A band is due to the spin-orbit-allowed transition, the C band is due to the dipole-allowed transition, while the B band is caused by the dipole-forbidden but vibration-induced transition. The C band has a triplet structure (the components are called C_1 , C_2 and C_3 bands) caused by the Jahn–Teller effect, while the A band has a doublet (A_1 and A_2) structure (Tsuboi *et al* 1973, Jacobs 1991).

Of the various s^2 ions (e.g. Ga^+ , In^+ , Tl^+ , Sn^{2+} , Pb^{2+} , Ge^{2+}) which are doped in potassium halide crystals, the Ge^{2+} ion is different from the others; the ion is expected to locate at the off-centre position in the substituting K^+ lattice site since the ionic radius of Ge^{2+} is 0.65 Å, which is considerably smaller than that of K^+ (1.33 Å). The luminescence of Ge^{2+} ions in KCl, KBr and KI has been studied (Zazubovich *et al* 1963, 1990a, 1990b, Kang *et al* 1988), but the optical absorption spectra have not been studied in detail. The off-centrality of the Ge^{2+} ions has been suggested from the luminescence spectra. Unlike the luminescence whose properties are determined by the Ge^{2+} ions after the optical excitation, the absorption spectra are expected to present more direct evidence of the off-centrality of the impurity ions in the ground state, i.e. before the optical excitation.

According to Baranov *et al* (1986) who studied the optically detected magnetic resonance (ODMR) spectra for Ge^{2+} ion in alkali halide crystals at 1.9 K, the Ge^{2+} ions have

a tetragonal symmetry. This symmetry was suggested to be due to the nearest neighbour cation vacancy. It has not, however, been clear whether the tetragonal symmetry is caused by the off-centring. In this paper we investigate the absorption spectra of Ge^{2+} centres in KCl and KBr crystals experimentally. Additionally, we calculate these absorption spectra using the Monte Carlo integration method and compare them with the observed spectra to clarify if the Ge^{2+} ions are at the on-centre positions.

2. Experimental procedure and results

Single crystals of KCl:Ge^{2+} and KBr:Ge^{2+} which were grown at the Institute of Physics, Estonian Academy of Science by Dr N Jaanson were used for the absorption measurements. The concentration of Ge^{2+} ions is approximately 10^{17} cm^{-3} . The crystals were heated at 550°C for 45 minutes and quenched to room temperature on a copper plate immediately before the absorption measurements. The absorption spectra were measured using a Shimadzu UV-3100 spectrophotometer in a temperature region of 15–300 K.

Figure 1 shows absorption spectra of a KCl:Ge^{2+} crystal at 16 and 287 K. The A_1 , A_2 , B, C_1 , C_2 and C_3 bands are observed at 276 nm (4.49 eV), 255 nm (4.86 eV), approximately 240 nm (5.16 eV), 231.1 nm, (5.365 eV), 219.0 nm (5.661 eV) and 211.7 nm (5.856 eV), respectively, all at 16 K. The B band is not observed as a band with a peak but as a shoulder at the tail of the C_1 band. This band is observed to grow with increasing temperature. As shown in figure 2, the position of the C_2 band is rather nearer the C_3 band than the C_1 band at low temperatures, but it shifts towards the C_1 with increasing temperature and locates at the middle of the C_1 and C_3 bands. Such behaviour has never been observed in the Sn^{2+} , Pb^{2+} , Ga^+ , In^+ and Tl^+ centres (Fukuda 1964, 1969); the C_2 band locates in just the middle of the C_1 and C_3 bands in these s^2 centres even if the temperature is changed. Figure 3 shows the temperature dependence of the distance between the C_1 and C_2 band peaks and the distance between the C_2 and C_3 band peaks. The former distance is observed to decrease with increasing temperature, while the latter is seen to increase. The increase of the C_2 – C_3 splitting with temperature almost agrees with the temperature dependence expected from the Jahn–Teller effect (Toyozawa and Inoue 1966, Fukuda 1969). In the other s^2 centres, not only the C_2 – C_3 splitting but also the C_1 – C_2 splitting has been observed to exhibit temperature dependence due to the Jahn–Teller effect (Fukuda 1969, Tsuboi *et al* 1973, Gannon and Jacobs 1975, Tsuboi, unpublished).

Similar absorption spectra are observed in KBr:Ge^{2+} with a well-resolved triplet structure of the C band as shown in figure 4. The KBr:Ge^{2+} spectrum is located at lower energy than that of KCl:Ge^{2+} . The A_1 , A_2 , B, C_1 , C_2 and C_3 bands are observed at 297 nm (4.17 eV), 283 nm (4.38 eV), approximately 267 nm (4.64 eV), 256.3 nm (4.837 eV), 245.5 nm (5.050 eV) and 237.0 nm (5.231 eV), respectively, all at 16 K. Unlike an asymmetric triplet-structured C band in KCl:Ge^{2+} where the C_3 band is the highest of the three components, an approximately symmetric C band is observed in KBr:Ge^{2+} since the C_3 band has the same peak height as the C_1 band. As in the case of KCl:Ge^{2+} , the C_2 – C_3 band splitting is smaller than the C_1 – C_2 splitting at low temperatures. The C_2 band, however, shifts toward the C_1 band with increasing temperature as shown in figure 5, resulting in the C_1 – C_2 splitting being smaller than the C_2 – C_3 splitting at high temperatures in KBr:Ge^{2+} .

In figure 6, we have plotted the temperature dependence of the half width of the C band in KCl:Ge^{2+} and KBr:Ge^{2+} together with that in RbCl:Sn^{2+} and RbBr:Sn^{2+} . It was found when the temperature is increased from 16 K to 300 K, the absorption bands in the Ge^{2+}

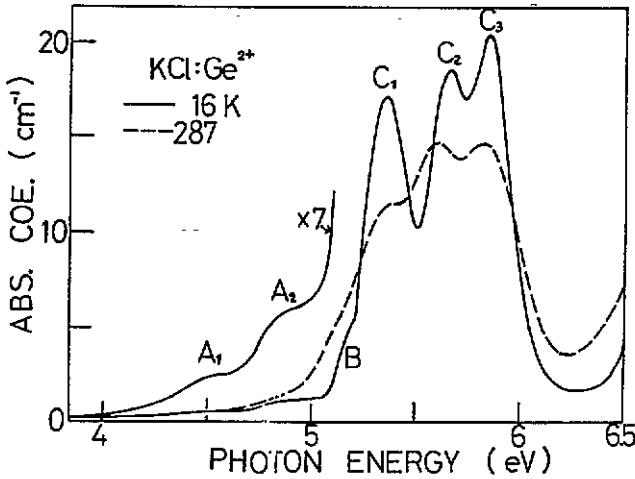


Figure 1. Absorption spectra of a $\text{KCl}:\text{Ge}^{2+}$ crystal at 16 K (solid curve) and 290 K (broken curve). ABS. COE. means the absorption coefficient.

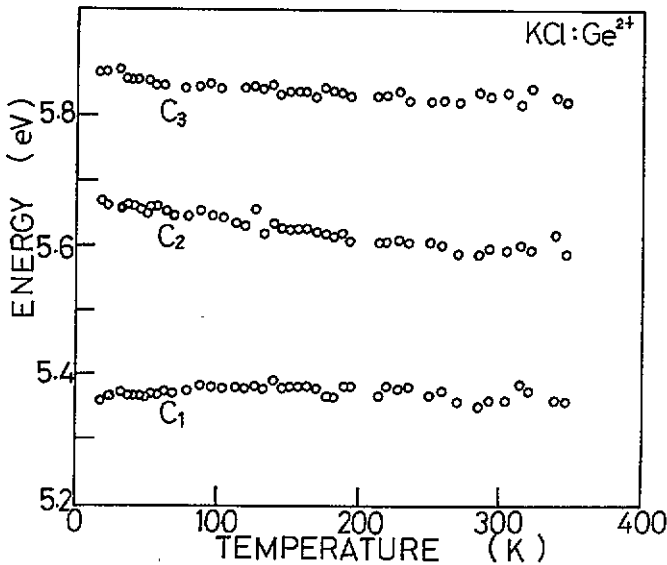


Figure 2. Temperature dependence of the peak positions of the three components of the C band in $\text{KCl}:\text{Ge}^{2+}$.

centre broaden by a very small amount, contrary to the cases of the other s^2 ion centres. For example, the bandwidth (i.e. half width) of the C band increases by about 1.4 times in Sn^{2+} centres in KCl, KBr, KI, RbCl and RbBr with increasing from 16 K to 300 K (Tsuboi *et al* 1973, Tsuboi and Hori 1992), while the bandwidth of the C band increases by about 1.06 times in the Ge^{2+} centres.

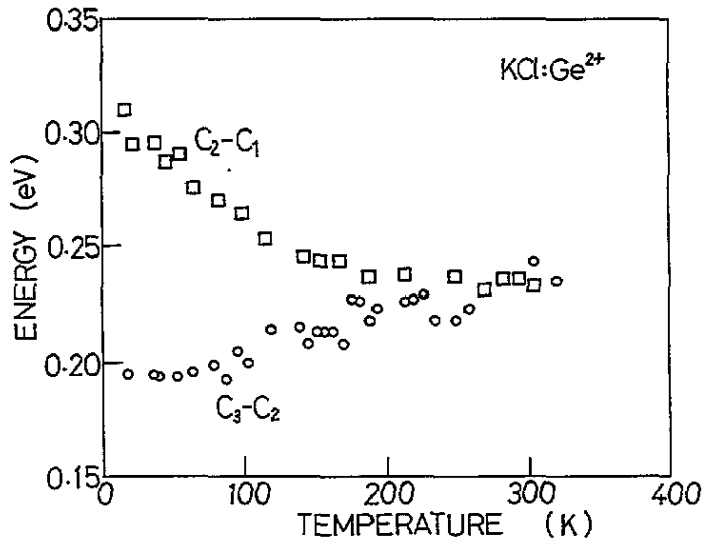


Figure 3. Temperature dependence of the C_2-C_1 and C_3-C_2 band splittings in $KCl:Ge^{2+}$.

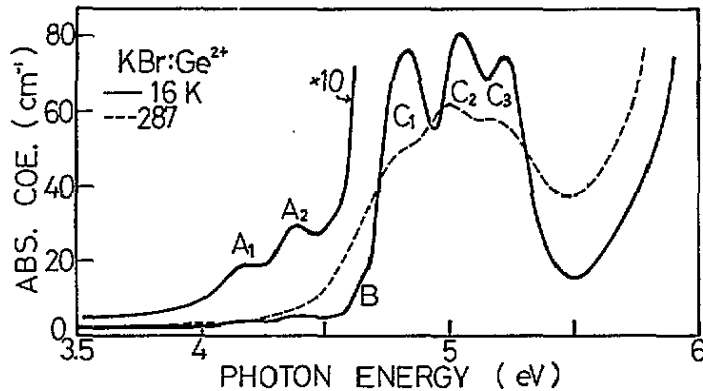


Figure 4. Absorption spectra of a $KBr:Ge^{2+}$ crystal at 16 K (solid curve) and 287 K (broken curve).

3. Monte Carlo simulations of the absorption spectra

The Hamiltonian for the $(a_{1g})(t_{1u})$ excited state of Ge^{2+} centre is given by

$$H = H_0 + H_{ee} + H_{so} + H_{eL} + H_{CF}$$

where H_0 is the sum of the kinetic energy of the two molecular electrons and their potential energy due to the central and surrounding ligand ions, H_{ee} is the Coulomb repulsion energy between the two electrons, H_{so} is the spin-orbit interaction, H_{eL} is the linear electron-lattice interaction with the $A_{1g}(Q_1)$, $E_g(Q_2, Q_3)$ and $T_{2g}(Q_4, Q_5, Q_6)$ lattice vibrational modes (Toyozawa and Inoue 1966, Jacobs 1991), and H_{CF} is the contribution from the electrostatic crystal field of tetragonal symmetry, which is assumed to be due to an off-centrality of the Ge^{2+} ion.

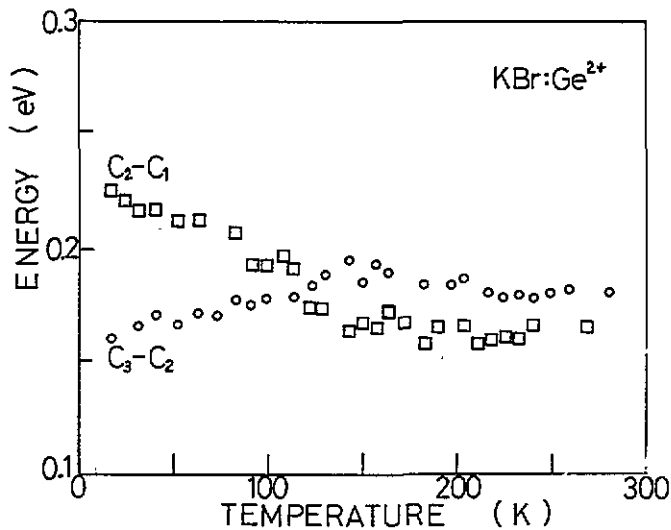


Figure 5. Temperature dependence of the C_2-C_1 and C_3-C_2 band splittings in $KBr:Ge^{2+}$.

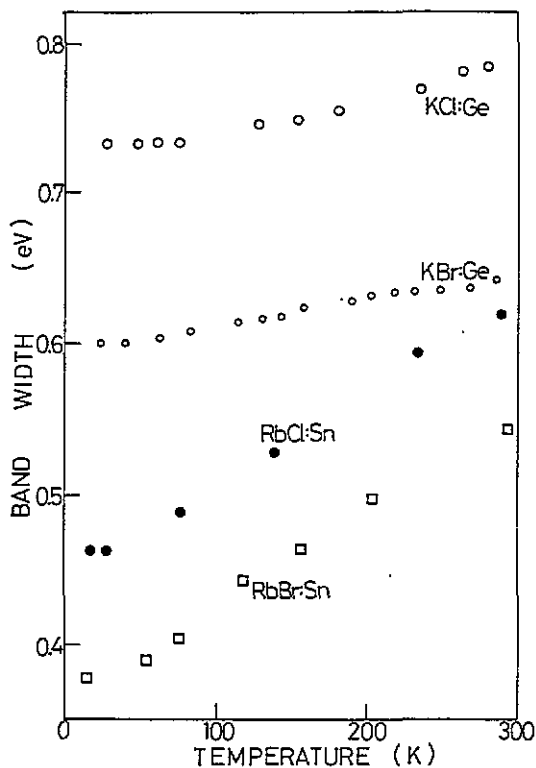


Figure 6. Temperature dependence of the C band width in $KCl:Ge^{2+}$, $KBr:Ge^{2+}$, $RbCl:Sn^{2+}$ and $RbBr:Sn^{2+}$.

Table I. Hamiltonian for the $(a_{1g})(t_{1u})$ state (after Jacobs 1991).

	$ \Gamma_1^- \rangle$		$ \Gamma_4^- (^3T_{1u}) \rangle$		$ \Gamma_3^- \rangle$
$(\Gamma_1^- $	$-G - \zeta + E_0$	0	0	0	$\sqrt{\frac{2}{3}} b Q_2$
		$E_A - \frac{b}{2}(Q_2 - Q_3/\sqrt{3}) + A$	$-\frac{c}{2} Q_6$	$-\frac{c}{2} Q_5$	$-\frac{c}{2} Q_4$
$(\Gamma_4^- (^3T_{1u}) $			$E_A + \frac{b}{2}(Q_2 - Q_3/\sqrt{3}) + A$	$-\frac{c}{2} Q_4$	$-\frac{c}{2} Q_5$
			$E_A - \frac{b}{\sqrt{3}} Q_3 - 2A$	$ic Q_6$	0
$(\Gamma_3^- $		(Complex conjugate)		$E_B - \frac{b}{\sqrt{3}} Q_3 - 2A$	$-\frac{b}{\sqrt{3}} Q_2$
					$E_B + \frac{b}{\sqrt{3}} Q_3 + 2A$

	$ \Gamma_3^- \rangle$	$ \Gamma_4^- (^1T_{1u}) \rangle$
$ \Gamma_1^- \rangle$	$\sqrt{\frac{2}{3}}cQ_4$ $i\frac{b}{2}(Q_2 + \sqrt{3}Q_3) - i3A$	0 $\xi\lambda/\sqrt{2}$
$ \Gamma_4^- (^3T_{1u}) \rangle$	$i\frac{c}{2}Q_6$ $i\frac{b}{2}(Q_2 - \sqrt{3}Q_3) + i3A$	0 $\xi\lambda/\sqrt{2}$
$ \Gamma_3^- \rangle$	$-i\frac{c}{2}Q_5$ $-\frac{c}{2}Q_4$ $\frac{2\sqrt{3}}{c}Q_4$ $E_B - \frac{b}{2}(Q_2 - Q_3/\sqrt{3}) + A$	$\sqrt{\frac{2}{3}}cQ_6$ $i\frac{c}{2}Q_5$ 0 $-\frac{c}{\sqrt{3}}Q_6$ $\frac{c}{2}Q_5$
$ \Gamma_5^- \rangle$	$E_B + \frac{b}{2}(Q_2 + Q_3/\sqrt{3}) + A$	0 0 0 0
$ \Gamma_4^- (^1T_{1u}) \rangle$	(Complex conjugate)	$E_c + \frac{2}{\sqrt{3}}b'Q_3 + 4A$

The Hamiltonian H is expressed by a 12×12 matrix (Jacobs 1991), leading to

$$H = aQ_1\mathbf{1} + H'$$

where $\mathbf{1}$ is a unit matrix of 12×12 and H' is given by table 1. The parameter A appearing in table 1 reflects the strength of the tetragonal crystal field in H_{CF} (Sivasankar *et al* 1982, Jacobs 1991), a , b and c are the linear electron–lattice coupling constants to the A_{1g} , E_g and T_{2g} vibrational modes for the triplet spin state, respectively, while b' and c' are the coupling constants for the singlet spin state (regarding the other parameters, see Jacobs (1991)).

Using the semiclassical Franck–Condon approximation, the lineshape of the absorption due to the $(a_{1g})^2 \rightarrow (a_{1g})(t_{1u})$ transition (the ground state is non-degenerate) is given by

$$F(E) = \sum_{j=1}^{12} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} (\pi kT^*)^{-3} \exp[-U_g/kT^*] (1/3) \times (|c_{10,j}|^2 + |c_{11,j}|^2 + |c_{12,j}|^2) \\ \times \delta(E - (U_e - U_g)) dQ_1 dQ_2 \dots dQ_6$$

where $c_{i,j}$ are elements of transformation matrix which diagonalizes the Hamiltonian H (Sivasankar *et al* 1982), U_g and U_e are the adiabatic lattice potential energy surfaces for the ground and excited states, respectively, E is photon energy, and T^* is the effective temperature which is connected with the crystal temperature T by the following relation

$$2kT^* = h\nu_{\text{eff}} \coth(h\nu_{\text{eff}}/2kT)$$

where ν_{eff} is an average frequency for the vibrational modes (Jacobs 1991). The ν_{eff} value determines the amount of band broadening due to the increase of crystal temperature.

We have chosen the normalization of $(Q_1, Q_2, Q_3, Q_4, Q_5, Q_6)$ such that the potential energy of the ground state becomes (Toyozawa and Inoue 1966, Cho 1969)

$$U_g = k_g Q^2 \quad \text{with} \quad k_g = 1$$

where

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

The excited-state potential U_e is expressed by

$$U_e = k_e Q^2 + E_j(Q)$$

where $E_j(Q)$ ($j = 1, 2, \dots, 12$) is the eigenvalue of the 12×12 Hamiltonian matrix H , and k_e is a parameter which is related with the force constant in the excited-state parabola and determines the curvature of the potential curve in the configuration coordinate diagram (Honma 1969).

We calculate the absorption lineshape, $F(E)$, by means of the Monte Carlo integration method to evaluate the integral over six coordinates Q_1 to Q_6 as was done previously (Cho 1969, Tsuboi and Hori 1992). In the calculation we used 500 000 sets of six random numbers Q_1, Q_2, Q_3, Q_4, Q_5 and Q_6 . We have calculated the absorption lineshape using various values of the a, b, b', c, c', A and k_e parameters. If the c value is smaller than about $0.5 \text{ eV}^{1/2}$, the B band was found to be immersed under the tail of the C_1 band, while as the c value is increased, the B band appears as a shoulder at the C_1 -band tail. As the c' value

is increased, the splitting among the C_1 , C_2 and C_3 bands becomes wide, together with the broadening of these bands. The increase of the negative A value gives rise to a wide splitting of the C_1 band from the C_2 and C_3 bands, keeping the C_2 – C_3 splitting constant. On the other hand, if we take a positive value for A , the C_3 band is separated from the C_2 band with an increase in the absolute value, keeping the C_1 – C_2 splitting constant. If we assume $A = 0$, we obtain the same amount between the C_1 – C_2 splitting and that of the C_2 – C_3 . It is found that we obtain an asymmetric C-band lineshape with different peak heights between the C_1 and C_3 bands if we assume that k_e is not equal to k_g . The lineshape is changed by the relative value between k_e and $k_g (= 1)$; the C_1 band becomes lower than the C_3 band when $k_e < k_g$, while the reverse is obtained when $k_e > k_g$.

Figure 7 shows examples of the calculated absorption curves $F(E)$ at 16 and 287 K for $KCl:Ge^{2+}$, together with an observed absorption spectrum at 16 K for comparison. The calculated curve is shown normalized to the peak of the C_2 band of the observed spectrum. The observed spectra of the A, B and C bands were obtained after subtracting the background. The calculation for a lineshape at 16 K was made using values of $\lambda = 0.35$, $a^2 = 0.13$ eV, $b^2 = b'^2 = 0.70$ eV, $c^2 = 1.00$ eV, $c'^2 = 1.00$ eV, $A = -0.055$ eV and $k_e = 0.50$, $E_A = 4.66$ eV, $E_B = 4.97$ eV and $E_C = 5.63$ eV. For the average frequency ν_{eff} , we used a value of $\nu_{\text{eff}} = 1.07 \times 10^{13}$ s $^{-1}$, which was estimated by taking into account the amount of the C-band broadening observed by the increase of temperature (figure 6). The calculated curve for 287 K was obtained using the same values for the parameters as was used for 16 K except for the A value. If we use the same $A = -0.055$ eV, we obtain equal values of the C_1 – C_2 splitting between the two temperatures, and the C_2 – C_3 splitting becomes large at 287 K. These are not in agreement with the experiment. If the A value is decreased, the C_1 – C_2 splitting is decreased. Thus, we chose a small value of $A = -0.035$ eV to fit the experimental result that the C_1 – C_2 splitting is the same as the C_2 – C_3 one at 287 K. The calculated absorption curves are similar to the observed spectra at 16 and 287 K.

Similarly, we calculated various absorption curves $F(E)$ for $KBr:Ge^{2+}$ using various combinations in values of the parameters. The lineshape calculated for 16 K is shown in figure 8. The lineshape was obtained using values of $\gamma = 0.50$, $a^2 = 0.15$ eV, $b^2 = b'^2 = 0.40$ eV, $c^2 = 1.00$ eV, $c'^2 = 1.50$ eV, $A = -0.03$ eV, $k_e = 1.30$ and $\nu_{\text{eff}} = 1.06 \times 10^{13}$ s $^{-1}$. $E_A = 4.32$ eV, $E_B = 4.50$ eV and $E_C = 5.03$ eV. It was found that we have to assume that $k_e < k_g$ for $KCl:Ge^{2+}$, while $k_e > k_g$ for $KBr:Ge^{2+}$, since the C_1 band is lower than the C_3 band in KCl but not in KBr . As seen in figure 4, the overlapping of the D band, which is expected to locate at high-energy side of the C band (Ranfagni *et al* 1983), is strong at high temperatures such as 287 K. This makes it difficult to subtract the background due to the D band. Therefore we have not made a comparison between the calculated and observed curves of $KBr:Ge^{2+}$ at 287 K.

4. Discussion

We have observed that the C_1 – C_2 splitting is different from that of C_1 – C_3 in Ge^{2+} centres in KCl and KBr . Such a difference has not been observed in other s^2 ion centres such as Tl^+ and In^+ . The divalent Sn^{2+} ion is accompanied by a charge compensating vacancy, therefore we expect that the vacancy gives rise to the difference between the C_1 – C_2 and C_2 – C_3 splittings. However, the C_1 – C_2 splitting is the same that of C_2 – C_3 in alkali halides doped with Sn^{2+} ions (Fukuda 1969, Tsuboi *et al* 1973). From these results, it is suggested

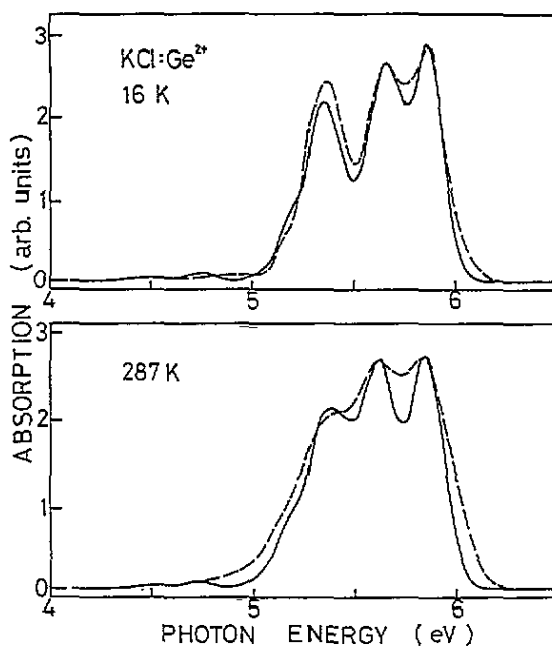


Figure 7. Calculated (solid curve) and observed (broken curve) absorption spectra of KCl:Ge^{2+} at 16 K and 287 K (see text).

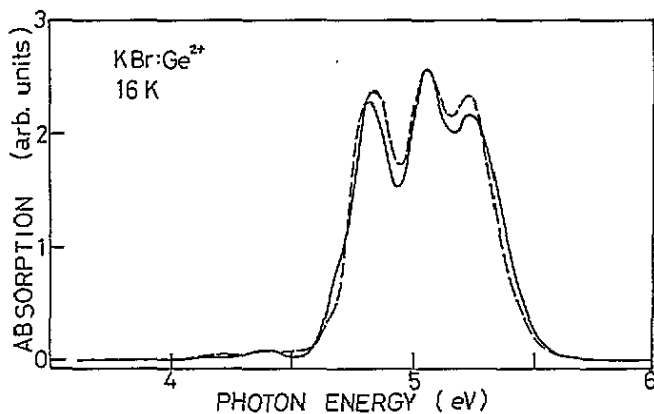


Figure 8. Calculated (solid curve) and observed (broken curve) absorption spectra of KBr:Ge^{2+} at 16 K.

that the vacancy is not predominant in inducing the difference between the C_1 - C_2 and C_2 - C_3 splittings observed in Ge^{2+} centres in KCl and KBr. Thus, the H_{CF} parameter A in the Hamiltonian H' is confirmed to be caused by the off-centre position of the Ge^{2+} ion.

The amount of the C_1 - C_2 splitting becomes almost equal to that of the C_2 - C_3 splitting with increasing temperature in KCl:Ge^{2+} and KBr:Ge^{2+} , suggesting that the tetragonal crystal field becomes weak at high temperatures. This behaviour is understood as follows. At low temperatures such as 16 K, the Ge^{2+} ion is at the off-centre position. However,

like most off-centred ions, as the temperature is increased, the Ge^{2+} ion does not remain in the off-centre position but moves over the off-centre potential barrier by a thermal energy process. At high temperatures, the Ge^{2+} ion can move freely within the substituting K^+ lattice site, resulting in a situation in which the average position is near the centre of K^+ position, i.e. the Ge^{2+} ion behaves as if it is an on-centred ion.

The C_1 , C_2 and C_3 peak-positions in the calculated lineshape of KBr:Ge^{2+} and KCl:Ge^{2+} at 16 K agree with the observed ones. At 287 K, however, both the C_2 and C_3 peak-positions in KBr:Ge^{2+} are deviated by 0.062 eV to the high-energy side from the observed ones. On the other hand, the C_1 , C_2 and C_3 peak-positions at 287 K in KCl:Ge^{2+} are almost in agreement with the observed ones. In KBr:Ge^{2+} , a tail is observed above 5.5 eV at 16 K. This tail shifts towards the low energy and approaches the C band with increasing temperature (see figure 4). Such a high-energy tail is also observed above 6.4 eV in KCl:Ge^{2+} . Contrary to the case of KBr, the tail of KCl does not show a large red-shift which gives rise to an overlapping with the C_3 band. The tail is believed to arise from the charge-transfer D band. In the present calculation we have neglected the presence of the D band. The disagreement of the C_2 and C_3 peak-positions in KBr:Ge^{2+} at 287 K between the calculation and observation seems to be improved by including the D-band state in the Hamiltonian H' . The detailed electronic state of the D band has not been established yet. In future we will consider, to get a more satisfactory result of the calculated lineshape, the interaction of the $(a_{1g})(t_{1u})$ state with its high-energy D state.

5. Summary

Unlike the cases of other s^2 centres (e.g. Ga^+ , In^+ , Sn^{2+} , Tl^+ , Pb^{2+}) where the C_2 band is located at the middle point of the C_1 and C_3 bands, we have observed in Ge^{2+} centres in KCl and KBr that the C_1 band is widely separated from the C_2 band at low temperatures when compared with the C_2 – C_3 splitting, and that the C_1 – C_2 splitting decreases with increasing temperature. At high temperatures such as 300 K, the C_1 – C_2 splitting was observed to be almost equal to that of C_2 – C_3 as in the cases of the other s^2 centres. Comparing the observed spectra with the absorption lineshapes calculated using the linear electron–lattice interaction and taking into account a tetragonal crystal field around Ge^{2+} ions, we have concluded that Ge^{2+} ion is at the off-centre position in the substituting K^+ ion site at low temperatures, while it is displaced towards the on-centre position by the thermal energy with increasing temperature. The temperature dependence of the triplet structure of the C band has been explained by taking into account both the off-centre effect and Jahn–Teller effect. The asymmetry of the C band has been observed to be stronger in KCl than KBr; i.e. the C_3 band is higher than the C_2 band in KCl, but not in KBr. Such asymmetry has been explained by a difference of the force constant between the excited-state and ground-state parabolae.

Acknowledgments

We thank Dr S Zazubovich for valuable discussions and Dr N Jaanson for growing crystals used in the present work. The present work was supported by the Grant-in-Aid from the Japanese Ministry of Education and Science.

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