Monte Carlo simulation of the absorption spectra of Tl^{+} ions in KMgF$_{3}$ crystals

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Abstract. The absorption spectrum of Tl$^+$ ions in crystals of KMgF$_3$ has been calculated in the region of bands A, B and C by means of the Monte Carlo integration method assuming a linear electron–lattice interaction and a cubic crystal field. The calculated spectrum at 10 K is in good agreement with the experimentally observed absorption. The results confirm that the Tl$^+$ impurity substitutionally replaces the K$^+$ ion and therefore it is in a cubic field in the KMgF$_3$ lattice. Unlike the s^2 ions in alkali halide crystals, the force constant of the excited-state parabola for Tl$^+$ ions in KMgF$_3$ was concluded to be larger than that of the ground-state parabola.

1. Introduction

Alkali halide crystals containing small amounts of Tl$^+$-like ions with an s^2 ground-state electron configuration exhibit three absorption bands due to the $(a_{1g})^2 \rightarrow (a_{1g})(t_{1u})$ electronic transition of the impurity (Ranfagni *et al* 1983, Henderson and Imbusch 1989, Jacobs 1991). They have been labelled bands A, B and C in order of increasing energy. There is a considerable amount of information on the absorption spectra of Tl$^+$-like ions in various alkali halide crystals. However, there are few reports on the spectra of Tl$^+$-like ions in ionic crystals other than alkali halides.

Recently the optical absorption spectra of Tl$^+$ ions have been measured in KMgF$_3$ crystals by Scacco *et al* (1993). Unlike the alkali halides, the bands A, B and C have been observed in the vacuum ultraviolet spectral region. The whole spectra are similar to those of Tl$^+$ ions and Tl$^+$-like ions (e.g. Ga$^+$, In$^+$, Sn^{2+} and Pb^{2+}) doped in alkali halide crystals if the peak positions of the absorption bands are neglected. For example, band C is more intense than band A, band B is much weaker than the others, and each of these bands shows a multiplet structure. However, unlike bands A and C observed for almost all alkali halides (Fukuda 1969, Jacobs 1991) with the exception of KF (Mayer *et al* 1975), it is observed that for KMgF$_3$ that, firstly, in band A the low-energy component A$_1$ is more intense than the high-energy component A$_2$ and, secondly, in band C the intensities of the components C$_1$, C$_2$ and C$_3$ decrease with increasing peak energy at low temperatures.

The present work has been undertaken to explain the reason why such different structures appear for Tl$^+$ ions in KMgF$_3$. Here the absorption spectrum is derived from a theoretical calculation using a Monte Carlo simulation.

The Tl$^+$ ion is believed to be substitutionally located at the K$^+$ ion position in the KMgF$_3$ lattice, because the two ion radii are close to each other (K$^+$, 1.33 Å; Tl$^+$, 1.44 Å). Therefore the symmetry of the Tl$^+$ centre is believed to be cubic. Since this symmetry has not been confirmed yet, the problem will be considered in this work.

2. Results of calculation and discussion

The Hamiltonian for the $(a_{1g})(t_{1u})$ excited state of the Tl^+ centre with cubic symmetry is given by

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

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 (Cho 1969, Toyozawa and Inoue 1966, Jacobs 1991). The Hamiltonian H is expressed by a 12×12 matrix (Tsuboi and Kamewari 1994).

The absorption lineshape $F(E)$ is calculated by means of the Monte Carlo integration method to evaluate the integral over six coordinates (from Q_1 to Q_6) using the method recently described by Tsuboi and Kamewari (1994). In the calculation we used 200 000 sets of six random numbers Q_1, Q_2, Q_3, Q_4, Q_5 and Q_6. The absorption lineshape has been calculated using various values of the E_A, E_B, E_C, a, b, b', c, c' and k_e parameters, where E_A, E_B and E_C are the energies of the excited states, A, B and C, respectively, relative to the ground state $^1A_{1g}$. The parameters a, b and c are the linear electron–lattice coupling constants to the A_{1g}, E_g and T_{2g} vibrational modes, respectively, for the triplet sign state, while b' and c' are the coupling constants for the singlet spin state, and k_e is the force constant in the excited-state parabola where the force constant k_g of the ground-state parabola is assumed to be $k_g = 1$.

In order to optimize the agreement between the calculated lineshape and the lineshape observed at 10 K, we first selected the values of E_A, E_B, E_C, ζ (spin–orbit splitting) and λ (a parameter which depends on the difference between radial wavefunctions of the singlet and triplet states) to fit at the same time the positions of bands A, B and C and their intensity ratios to the experimental results. At this stage we did not try to fit the width and the structure of each band. The following values were obtained: $E_A = 6.39$ eV, $E_B = 7.23$ eV, $E_C = 7.92$ eV, $\zeta = 0.84$ eV and $\lambda = 1.295$. It must be noted that the values for E_A, E_B and E_C do not coincide with the energies of the peak positions of bands A, B and C, respectively.

Next we concentrated our attention on the bandwidth and structure, which are influenced by the electron–lattice coupling constants a, b, b', c and c', the average frequency ν_{eff} of the vibrational modes and the force constant k_e. Several runs of calculations were performed by changing the values of all such parameters, and finally we obtained a calculated spectrum at 10 K by choosing values of $a^2 = 0.1$ eV, $b^2 = b'^2 = 0.2$ eV, $c^2 = c'^2 = 1.6$ eV and $k_e = 2.1$, and using for ν_{eff} the value 150 cm^{-1} estimated from the temperature dependence of the half-width of band C_1 reported by Scacco *et al* (1993). The whole spectrum is shown in figure 1, while figures 2, 3 and 4 display the enlarged calculated lineshapes of bands A, B and C, respectively, in comparison with the experimental data. The positions and lineshapes of all the observed bands are well reproduced, whereas the agreement between calculation and experiment is less satisfactory for the band width. Such a good fit of the calculated lineshapes to the observed lineshapes suggest that the symmetry of the Tl^+ ion is cubic, leading to confirmation that the Tl^+ ion is substitutionally located at the K^+ ion positions in the $KMgF_3$ lattice.

An asymmetric band-C lineshape with different peak heights for components C_1 and C_3 is obtained, assuming k_e is not equal to $k_g(= 1)$. Component C_1 becomes less intense than component C_3 when k_e is less than k_g, and vice versa. The same result is found for
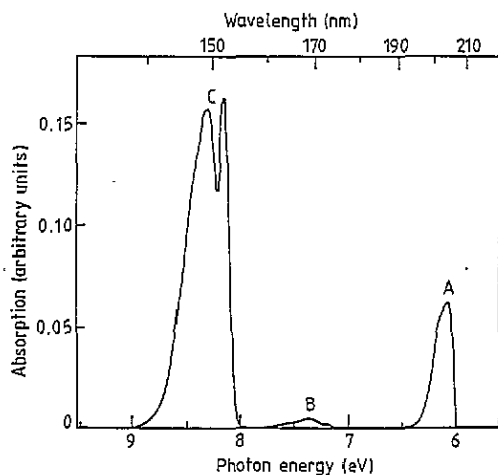
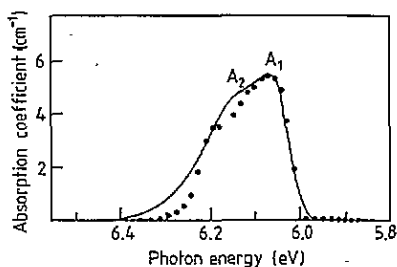**Figure 1.** Calculated absorption spectrum of a KMgF₃:Tl⁺ crystal at 10 K.

Figure 2. Lineshape (——) of band A, taken from figure 1, compared with the experimental data (•). The two spectra are normalized at the highest peak height.
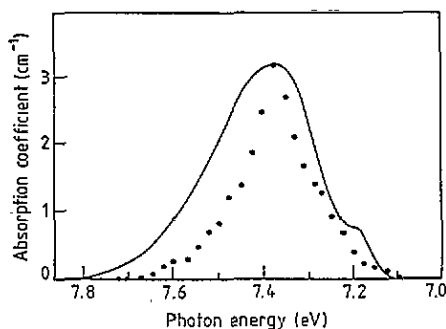

Figure 3. Lineshape (——) of band B, taken from figure 1, compared with the experimental date (•). The two spectra are normalized at the highest peak height.
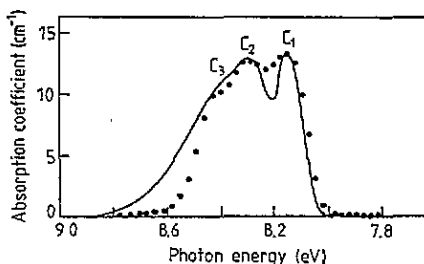
Figure 4. Lineshape (——) of band C, taken from figure 1, compared with the experimental data (•). The two spectra are normalized at the highest peak height.

the doublet-structured band A; component A_1 is less intense than component A_2 when k_e is less than k_g, and the reverse is true in the opposite case. Therefore the k_e-value has been chosen to be larger than the k_g-value for KMgF₃:Tl⁺.

The unusual asymmetric structure of band A with a more intense low-energy component than the high-energy component has been observed for not only KMgF₃ but also KF. The Tl⁺ ions in these crystals are surrounded by nearest-neighbour F⁻ ions whose ionic radius is 1.36 Å, i.e. the Tl⁺ ion is surrounded by the smaller halide ions. When the Tl⁺ ion and the other s^2 ions such as In⁺ and Pb²⁺ are surrounded by nearest-neighbour halide ions whose ionic radii are larger than those of the s^2 ions (In⁺, 1.3 Å; Pb²⁺, 1.21 Å; Cl⁻, 1.81 Å; Br⁻, 1.95 Å; I⁻, 2.16 Å), such an asymmetric structure has not been observed but component A_1 is less intense than component A_2. Therefore, it is suggested that one of the reasons why k_e is larger than k_g for KMgF₃ is that the Tl⁺ ion is surrounded by smaller

nearest-neighbour ions.

In the lineshape calculation, only a doublet structure is evidenced for band A. This does not agree with the experimental data which show a non-pronounced shoulder on the high-energy side of component A_1. On the basis of this shoulder, a proposal for a triplet structure of band A was put forward, which has to be reconsidered because of the calculation results.

In the present calculation the presence of band D has been neglected. This band, which is caused by charge transfer, has been observed at about 138 nm (8.99 eV), i.e. at a higher energy than band C. Since the calculated lineshape of band C shows a long tail on its high-energy side, probably the disagreement with the data would be less pronounced by including the band D state in the Hamiltonian. In the near future, we shall try to couple a theoretical investigation on the electronic state of band D with a more detailed observation of its spectral features.

Acknowledgments

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