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Lattice relaxation of luminescence centres of the X -line emission of ns^2 impurity ions in alkali halides; anomalous geometry of the impurity centre in the excited $nsnp$ state

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Abstract

Clear evidence was found that in the active centre from which the X -line emission of ns^2 impurities in alkali halides originates the excited impurity ion is statically displaced over an anomalously large distance in a direction which depends on the lattice structure. For fcc this is one of the (111) directions and the centre has trigonal symmetry, and for the bcc lattice it is one of the (001) directions and the symmetry is tetragonal. The displacement only occurs in the excited state and probably is a result of covalency effects. The study was performed using a readily available code for lattice relaxation around impurity ions. For the fcc lattice we have studied the relaxation of Ga^+ , In^+ and Tl^+ in KCl and of In^+ in KBr. For the bcc case we considered In^+ in high-pressure KCl. A comparison with well known experimental data for the three impurity ions and the good agreement found for both the T - and X -line emission wavelengths supports our theoretical results.

1. Introduction

In alkali halides containing ns^2 ions three main absorption bands are observed, called A, B and C [1, 2]. On excitation in the A band usually two emission lines are found, one called A_T with a short wavelength and one denoted A_X with a longer wavelength. By polarization measurements at low temperatures it was established that in the fcc lattice the A_T line originates from a centre with tetragonal symmetry and for A_X the centre symmetry is trigonal. In only a few papers is it mentioned that for the bcc lattice in contrast it is the A_T line which comes from a trigonal centre [3] and the A_X line from a tetragonal one.

For the fcc lattice it is widely accepted that the geometry of the tetragonal centre is such that two of the six neighbouring anions (say on the z -axis) are displaced away from the central

ion and at the same time the other four anions are displaced inward. The excited np orbital is then directed along the z -axis. In our recent study [4] of Tl^+ and In^+ centres in the fcc lattice it was shown that accurate relaxation studies can nicely explain the experimental data on the Stokes shift and some of the decay time characteristics. For the bcc lattice we have found that the trigonal-centre geometry is a distortion of the surrounding cube of eight anions in one of the (111) directions and so the np orbital in the excited state is directed in this direction. In the literature sometimes the characterization of this line is adapted to the centre symmetry and is called the A_X line. We shall use the oldest convention and call the line with the shortest wavelength the A_T line.

From the first observation of the X -line in 1930 up to the 1990s, many experimental and theoretical papers were devoted to searching for the structure of the centre responsible for this line. This was done almost exclusively for the fcc lattice. Apart from the centre symmetry (trigonal) the centre geometry remained unknown because the theoretical efforts could not explain experimental results. The main problem is the coexistence of two or more minima on the potential surfaces of the excited $nsnp$ state with the specified centre symmetry. By common consent [1] for heavy ions such as thallium, spin-orbit interaction could provide two coexisting minima in tetragonal Q_2 , Q_3 space. However the centre symmetries are found to be tetragonal and orthorhombic instead of tetragonal and trigonal. For lighter atoms such as indium and gallium second-order Jahn-Teller coupling to a product of the symmetrical distortion modes A_{1g} (Q_{1g}) and T_{2g} ($Q_{4,5,6}$) could provide a trigonal centre, but the coexistence with a tetragonal centre requires a sophisticated relation between certain parameters [5]. Because of the very large Stokes shift of the X -lines the required strength of the coupling to the T_{2g} mode had to be larger than that of the E_{2g} (Q_3) mode and that is unrealistic. In our view no real progress could be made because of the lack of lattice relaxation studies. With this in mind we have performed lattice relaxation studies on the standard coupling modes mentioned above. Additionally distortion modes were considered with odd symmetry, implying that the central ion is displaced from its position. Our motive was to explain *ab initio* the magnitude of the Stokes shift of the X -line and also why the X -line is absent from some crystals. We have chosen the following systems to investigate. (1) Fcc KCl with thallium, indium and gallium. The curious point is that here only gallium shows X -line emission. (2) Indium in high pressure KCl where the lattice type is bcc and X -line emission is observed. (3) Fcc KBr doped with indium was studied because X -line emission has also been detected here.

2. Theoretical methods

For our calculations we have used a lattice relaxation program kindly supplied by Schluger from the Department of Physics and Astronomy of University College London. The method follows an embedded cluster approach for the impurity centre: this centre is part of a molecular cluster of ions (called QC) of which the electronic structure is calculated using the HF-LCAO method. The cluster is embedded in a polarizable lattice, taken to be a cubic nano-cluster of $13 \times 13 \times 13$ unit cells for the fcc lattice and $19 \times 19 \times 19$ cells for the bcc lattice. In figure 1 the scheme of embedding is illustrated. In the spherical region I, the ions outside the cluster are relaxing point charges interacting with each other and the cluster via interatomic potentials in the Mott-Littleton model. The dipole polarizability of these ions is taken into account by the shell model. The ions in region II are non-polarizable and cannot relax. They serve to establish an approximation for the infinite lattice. With this approach it is possible to mimic the relaxation of hundreds of ions with a moderate amount of computer time: the calculation of the electronic structure of the quantum cluster which consists typically of some 20 ions. The program we have used is the Dcluster99 program [6], which interfaces the Gaussian98

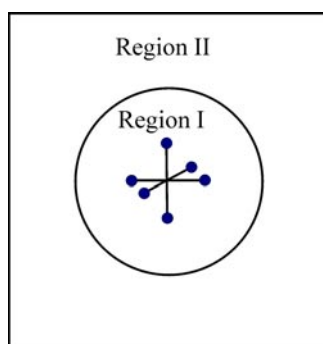


Figure 1. Embedded cluster regions of the Mott-Littleton lattice model. The point charges in region I can relax and interact with each other and the quantum cluster at the origin via interatomic potentials. The dipole polarizability of these ions is taken into account by the shell model. This region is spherical and contains typically some 1000 point charges. Those of region II are fixed and cannot polarize.

code [7] for the QC part with the Gulp code [8] for the Mott-Littleton part. The approach is similar to that used in [4] and the same inter-ionic potentials were used for the Gulp part. For the QC part the Gaussian basis sets for thallium and indium were as used in [4]. For gallium a small-core (ten electrons) ecp basis [9] was used, similar to those of thallium and indium.

3. Level structure

The excited $nsnp$ configuration has a spin singlet (1P) and a spin triplet level (3P), which in an octahedral site in the lattice become the $^1T_{1u}$ and $^3T_{1u}$ states. Spin-orbit interaction will mix these two states and the $^3T_{1u}$ level splits into four sublevels [1]. The lowest level is non-degenerate and is denoted by 3A_u . This level is metastable because the transition to the ground $^1A_{1g}$ (ns^2) state is strongly forbidden. The next higher level is the one which gives rise to the A band absorption and also the two emission lines. It is a triply degenerate level, which is denoted by $^3T_{1u}$ in the literature. It has a slight admixture of the $^1T_{1u}$ level by which electric dipole transitions are allowed. This level will split by the Jahn-Teller effect into a doublet and a singlet and we are interested in the position of these levels in comparison with the ground $^1A_{1g}$ (ns^2) level.

Because of the complicated emission spectra it is obvious that various ways of relaxation do exist. In this work we consider three types of relaxation. Figure 2 illustrates the three different modes of distortion of the lattice around the impurity for the fcc lattice and for the bcc lattice. First, we have the tetragonal mode (E_g symmetry) characterized by the parameters Q_2 and Q_3 [10]; only Q_3 is shown. This is the relaxation we considered in [4]. Secondly, we have the mode with the parameters Q_4 , Q_5 and Q_6 with symmetry type T_{2g} , of which only Q_4 is shown. To keep the drawing simple for the bcc lattice only the displacements of the top four anion neighbours are shown. The bottom displacements are obtained by inversion. The displacements of the other two components Q_5 and Q_6 are obtained by changing the axes. In our relaxation work we have modelled only the linear combination $Q_4 + Q_5 + Q_6$, which models the trigonal lattice distortion in one of the (111) directions. The Q_3 and Q_4 modes couple in first order with the electronic $nsnp$ state. The Q_D modes shown in figure 2 are odd-symmetry modes, which only couple in second and higher order but were found to be very probably the dominant modes for explaining the X-line emissions. The most important

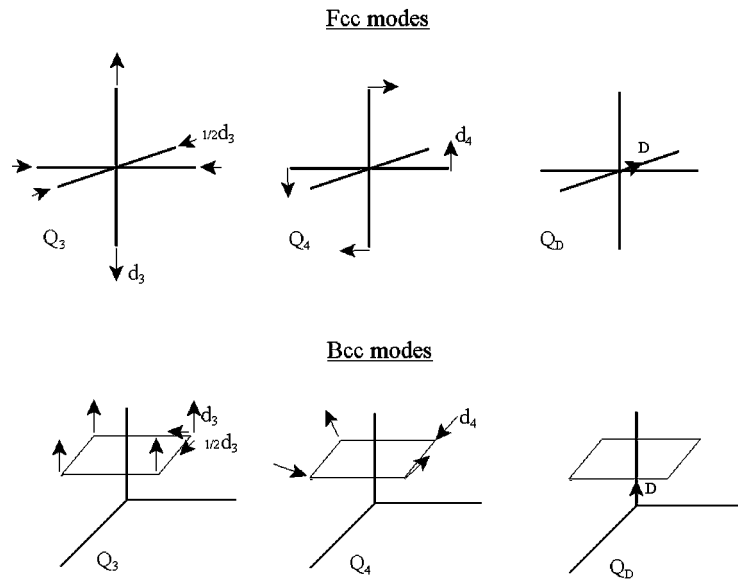


Figure 2. Distortion modes used in the relaxation studies. For the fcc lattice the Q_3 relaxation is performed just as indicated. The Q_4 mode however is combined with the Q_5 and Q_6 modes to obtain a distortion in the (111) direction. For the X -centre it is combined with the displacement mode Q_D . For the bcc lattice only the distortion of the upper four anions is shown. The bottom ones are obtained by inversion. Again the Q_4 mode is combined with Q_5 and Q_6 to obtain an outward displacement of $3d_4$ of the two ions on the (111) line and d_4 inward for the other six anions. The X -centre distortion is a combination of Q_3 and Q_D .

aspect is the displacement of the impurity ion from its central position. We have introduced the displacement parameter D for this mode. The modes are similar in fcc and bcc lattices. We emphasize the fact that the A_X line for the fcc lattice originates from a trigonal centre with a (111) displacement whereas for the bcc lattice the X -centre is tetragonal and the displacement is in one of the (001) directions. Evidence for this conclusion will be given in the following.

4. Results

In this section we only give details about the most important findings. The coupling to the Q_3 mode was extensively studied in [4] for KCl doped with thallium and indium. In that work it was found how important it is to include the spin-orbit interaction in a proper way for explaining the Stokes shift and the emission process of the A_T line. Here we are principally interested in the relaxation mode, which can explain the A_X emission line, and the total level structure is of minor importance, so we can greatly simplify the approach by neglecting the spin-orbit interaction. Actually mainly the results on thallium will be affected. We could correct for this to a certain extent by using the results given in [4]. With the constants calculated in that work we found that thallium in KCl indeed has a second minimum of orthorhombic symmetry but the depth is much smaller than that of the tetragonal centre. Therefore it is very unlikely that this effect can explain the X -line of thallium in the very similar KBr crystal. Unfortunately there is no X -line emission of thallium in KCl . Our earlier study on Q_3 linear coupling of thallium and indium in KCl was extended with the gallium case. The linear coupling to T_{2g} modes was studied for indium in KBr . The coupling was found to be much too small to

Table 1. Energy differences between the triplet $nsnp$ and the ns^2 states calculated in the HF-LCAO approach compared with experiment. The lattice relaxation was performed for the ns^2 state of the impurity. The effects of spin-orbit interaction were neglected. E_{corr} is the energy correction we shall add to the calculated emission energies after lattice relaxation in the $nsnp$ state.

Crystal	Ion	ΔE_{HF} (eV)	ΔE_{exp} [2] (eV)	E_{corr} (eV)
KCl (fcc)	Tl ⁺	5.23	5.03	-0.20
	In ⁺	3.73	4.33	0.60
	Ga ⁺	4.26	4.80	0.54
KCl (bcc)	In ⁺	3.84	4.43	0.59
KBr (fcc)	In ⁺	3.68	4.18	0.50

explain the X -line. A value of 0.4 eV was calculated for the Stokes shift compared with 1.8 eV found experimentally. Only the combination of these modes with the displacement mode Q_D was found to provide enough relaxation to lead to the very large Stokes shift. An important contribution to this shift originates from the raising of the ns^2 level by the displacement of the impurity ion. We shall give details of these findings below.

4.1. Absorption lines

For a comparison of the relaxation results with experiment it is necessary to compare the data for the HF-LCAO ns^2 to $nsnp$ (triplet) excitation energies of the impurity ions in a lattice relaxed for the ns^2 ground states with the experimental absorption energies. The point is that HF-LCAO in general provides energy differences which are smaller than experiment because of correlation effects. We will correct *ad hoc* the ns^2 to $nsnp$ energies after relaxation with those found before relaxation of the lattice for the $nsnp$ state. These corrections are found from table 1, where we list the ns^2 to $nsnp$ energies found from the HF-LCAO calculation before relaxation and those found from A-band absorption.

4.2. Lattice relaxation and emission lines

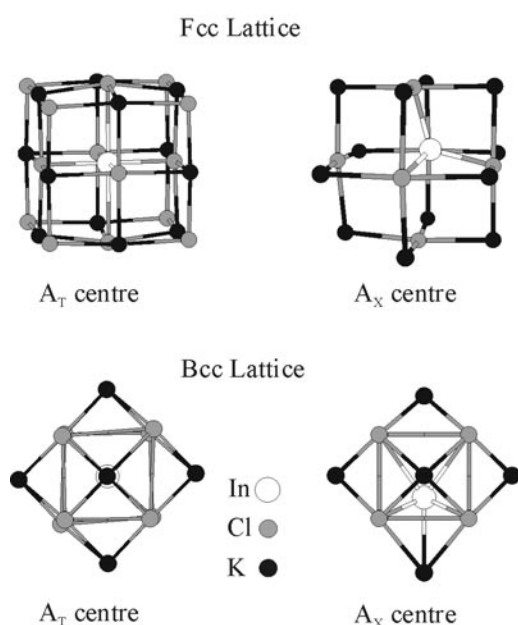
The embedded cluster calculations were performed on various molecular fragments. For the fcc lattice two clusters were used adapted to the relaxation type. For the tetragonal (Q_3) type mode an MCl_6K_{18} cluster was defined, where M is the impurity ion and we have the six nearest neighbours and twelve next-nearest neighbours. The six fourth-neighbour potassium ions, a lattice unit a_0 away on the x -, y - and z -axes, were added to have a better accommodation for the expected displacements of the neighbouring chlorine ions.

For the Q_4 , Q_D mode we have used just the MCl_6K_{12} cluster consisting of nearest and next-nearest neighbours. It was checked whether representing the rest of the lattice by relaxing point charges in the Mott-Littleton approach is good enough. This was done by repeating this relaxation using the former cluster of the Q_3 mode. A satisfactory agreement in relaxation was obtained. For the bcc lattice the same cluster fragment was used for the Q_4 as well as for the Q_3 , Q_D relaxation. It was the MCl_8K_{14} ionic cluster consisting of nearest-neighbour chlorines and next nearest and fourth-neighbour potassium ions. In this way accommodation was made for the expected Q_4 type relaxation in the (111) directions. In table 2, for all systems we studied, the results are listed of the distortion coordinates of the nearest-neighbour chlorine

Table 2. Distortion coordinates of the centre geometry for the A_T and the A_X lines. See figure 2 for the explanation of the symbols. All values are in Å.

Crystal	Ion	A_T centre		A_X centre ^a		D
		d_3 (e_{2g})	d_4 (t_{2g})	d_3^+/d_3^- (e_{2g})	d_4^+/d_4^- (t_{2g})	
KCl (fcc)	Tl ⁺	0.433	—	—	−0.128/−0.050	1.06
	In ⁺	0.485	—	—	−0.110/−0.054	1.08
	Ga ⁺	0.541	—	—	−0.036/−0.025	1.36
KCl (bcc)	In ⁺	—	0.095	−0.082/−0.034	—	0.86
KBr (fcc)	In ⁺	0.530	—	—	−0.133/−0.045	1.20

^a For the A_X centre the displacements d_3 and d_4 are listed for the positive and negative sides of the axes. This is a result of the displacement of the impurity ion from its centred position. The notation e_{2g} and t_{2g} actually does not apply here but is kept to show the relation with the modes of figure 2.

**Figure 3.** Final T - and X -centre geometries for the fcc and the bcc lattices. Indium in KCl was taken as an example. One can clearly see the anomalous large displacement (D) of the impurity ion in the X -centres. The displacement of the nearest neighbours is much smaller for the X -centres compared with the T -centres.

ions after relaxation of the fragment with the embedding procedure mentioned above (see also figure 2). Note the large displacements for the Q_3 mode in the fcc lattice for the A_T centre and the very large displacement, D , of the impurity ion from its centred position for the A_X line centres. This displacement only occurs in the excited state. The small value of d_4 for the bcc lattice is somewhat misleading. Actually the two chlorine ions on the (111) line move $3d_4$ outward and the other six ions move d_4 inward. The other displacements shown for the X -centres are relatively small. In figure 3 the final geometries of the nearest neighbours are given for the A_T and A_X line centres of indium in fcc and bcc KCl. In one picture an overview is given of the most important findings of this study.

Table 3. Relaxation energies for the A_T and A_X line centres and calculated energies of the corresponding emission lines compared with experiment. All values are in eV.

Crystal	Ion	A_T line			A_X line		
		E_{relax}	ΔE_{nsnp}	ΔE_{exp}^a	E_{relax}	ΔE_{nsnp}	ΔE_{exp}^a
KCl (fcc)	Tl ⁺	0.602	3.71	4.07	0.56	3.19	—
	In ⁺	0.676	2.95	2.90	0.578	2.51	—
	Ga ⁺	0.767	3.22	2.85	0.994	2.30	2.35
KBr (fcc)	In ⁺	0.649	2.88	2.86	0.585	2.36	2.40
KCl (bcc)	In ⁺	0.395	3.69	3.39	0.309	2.88	2.58

^a The experimental results except those of gallium are from [11]. The gallium results are from [12].

It is straightforward to obtain the relaxation energy from the difference in total energy between the unrelaxed (ns^2 state relaxed) and the relaxed lattice. Furthermore the new ns^2 energy level is calculated for the relaxed geometry. In this way an estimate is made of the energy of the emission lines. For a fair comparison with experiment we corrected these energies with E_{corr} presented in table 1. Results are listed in table 3. Overall a reasonable agreement between theory and experiment is observed, particularly for the A_X line. We shall now discuss briefly the differences between theory and experiment in more detail. (1) The small value of ΔE_{nsnp} for thallium compared with experiment is a consequence of the neglect of spin-orbit interaction, which counteracts the relaxation and would increase this energy difference [4]. (2) For the A_T line the Ga⁺ ion gives an unexpected large disagreement. Note also that here the relaxation energy of the X -centre is larger than that of the T -centre, in contrast to the other cases. It is a peculiar fact that we find that the minimum in the X -centre relaxation curve appears to be in most cases above that of the T -centre curve. This is completely in disagreement with the assumptions found in the literature, where the X -centre minimum is always assumed to be below the T -centre minimum. This assumption is a result of the very large Stokes shift measured and so is reflected in the low-lying X -centre minimum. We have found however that the large Stokes shift is mainly a result of the raising of the $^1A_{1g}$ (ns^2) ground-state level. (3) It is also remarkable that for indium in bcc KCl the agreement between theory and experiment is less (0.3 eV) than in the fcc phase. This applies for the A_T line as well as for the A_X line. The amount of disagreement is not large but moderate. It shows the limitations of this type of relaxation study. (4) A curious fact is also that in fcc KCl for Tl⁺ and In⁺ no X -line emissions were detected. This is in contrast with the very similar KBr crystal, where this line was detected for both ions.

5. Discussion and conclusions

In summarizing the results presented above it is very likely that the centre responsible for X -line emission always consists of an impurity centre displaced over a large distance from its centred position. Up to the present time no reference has been found for this huge change in geometry as an explanation of the large Stokes shift of the X -lines. Actually a new approach is required for interpreting the emission lines of ns^2 type ions. Lattice relaxation studies must play an important role in the search for the right geometry. The displacement of the impurity ion found in our study probably could be measured with ODMR-ENDOR. Work is in progress to try this [13]. The displacement found is very different from the off-centre positions reported

earlier in the literature [14]. These positions result from distortions of, say, the Q_3 mode, i.e. a small movement of the impurity ion perpendicular to the z -direction.

The embedded cluster approach with a basic HF-LCAO framework proves again to be a practical method to calculate this type of relaxation in the excited state of an impurity ion. From the results of indium in fcc and bcc KCl it is clear that the simple approach taken has systematic errors which depend on the lattice structure. This is not surprising but the amount of discrepancy is larger than expected. Clearly this has to be investigated further.

The major problem, which is left untouched, is the mechanism by which the A_X and A_T lines are emitted. This problem is directly related to the problem of coexistence of T and X minima mentioned above and the question of how the levels are populated. How can we explain the fact that Tl^+ and In^+ in fcc KCl do not show X -line emission whereas they do in KBr ? Also the appearance of X -line emission of In^+ in bcc KCl adds to this problem. We have seen above that the minima in energy for the X -line centres are mostly found above those of the T -line centres (for Tl^+ and In^+). The standard conclusion would be that non-radiative processes would populate only the lowest level and only A_T line emission would result. It is our view that an explanation of these problems cannot be found by considering only the final relaxation geometry. A *dynamical* viewpoint of the emission process is required. In view of this dynamical approach we shall discuss two important aspects of our relaxation studies, not mentioned so far. The first one is that, because the displacement mode distortion Q_D corresponds to higher-order coupling, the derivative of the energy to this mode coordinate is zero when relaxation starts. This is in contrast to the T -line modes, where the derivative is non-zero because of first-order coupling. The relaxation curves of the X -centre and the T -centre are therefore quite different. In time the X -centre relaxation curve is expected to be above the T -line curve (the relaxation proceeds more slowly). A second observation is that the final geometries of X - and T -line centres are so different that non-radiative processes between the two centres are slow. Only when relaxation starts and the distortions are small are there fast non-radiative transitions which depopulate the X -line centres, but these become slower and slower as relaxation proceeds. Using this dynamical picture there may be an explanation for the fact that for gallium in KCl the A_T line found theoretically is so different from experiment. From table 3 it is clear that in the relaxation process for this ion there is level crossing because the X -centre minimum is below the T -centre minimum. One may expect then three lines because the crossing point certainly will give an extra minimum. There is some evidence for this fact from the measurements reported in [12] where three lines are clearly observed. However the line intensities are puzzling. Also the fact that the A_X line is sometimes missing may be due to fast depopulation of the X -line geometry after absorption. The dynamic relaxation processes depend on the vibration frequencies of the centre. It is very hard to estimate values for the constants in the required rate equations and so, unfortunately, we cannot give more evidence for this theory.

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