

POSSIBLE SPLITTING OF ENERGY LEVELS OF ATOMS OR IONS IN OCTAHEDRAL CRYSTALS DUE TO SETS OF EQUIVALENT NEIGHBOURING DEFECTS

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ABSTRACT

Divalent ions when doped in alkali halide single crystals will go in alkali sites and form associate pairs with neighbouring cation vacancies or other impurity defects. As there will be sets of equivalent positions for such associated pairs, their energy levels will be degenerate. The reducible representations of these associated pairs involving first to sixth nearest neighbours have been reduced to the corresponding irreducible representations of the point group O_h , for cases having rock-salt structure as well as for cases having cesium chloride structure. It is pointed out that if there is a rapid hopping of the vacancies or the defects in the crystal one may expect because of the possible interactions in the system, a splitting of the energy levels of the pairs as indicated by the different irreducible representations. It is stated that this kind of splitting may be expected also in systems in which associated magnetic pairs are formed by two neighbouring spins.

THE introduction of a divalent ion in alkali halide single crystals causes a charge unbalance. Different charge compensations corresponding to different point symmetries have been reported.¹⁻³ The divalent ion may go into the alkali halide crystal in any of the following ways: (1) in the form of precipitated divalent ions, (2) in the cation lattice sites but isolated from one another and also far away from any defect thereby preserving a local cubic symmetry, or (3) in the form of associated pairs with the probable neighbouring alkali site vacancy defects. In the third case, for crystals having rock salt structure the divalent ion will have twelve equivalent first nearest neighbours (alkali vacancies), six equivalent second nearest neighbours, twenty-four third nearest neighbours, twelve fourth nearest neighbours, twenty-four fifth nearest neighbours and eight sixth nearest neighbours. The energy levels of pairs involving the first nearest neigh-

bours will be twelvefold degenerate, while those of the pairs involving second, third, fourth, fifth and sixth nearest neighbours will be sixfold, twenty-four fold, twelvefold, twenty-four fold and eightfold degenerate respectively. The wave functions of these pairs will form the basis for reducible representations of the octahedral point group. Following the general principles of group theory these can be reduced into the corresponding irreducible representations of the point group O_h . Table I shows the character table^{4, 5} for the point group O_h as well as the characters for the different reducible representations D of the associated pairs under consideration along with the irreducible representations into which the reducible

TABLE I

Character table for point group O_h and reduction of the reducible representations of the equivalent sets of associate pairs for rock-salt structure

O_h	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$3C_2$	$3C_2$	$6C_4$	$6C_2'$	Reduced representations
A_{1g}	1	1	1	1	1	1	1	1	1	1	..
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	..
E_g	2	-1	2	0	0	2	-1	2	0	0	..
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1	..
T_{2g}	3	0	-1	-1	1	3	0	-1	-1	1	..
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	..
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	..
E_u	2	-1	2	0	0	-2	1	-2	0	0	..
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1	..
T_{2u}	3	0	-1	-1	1	-3	0	1	1	-1	..
D_{12}^1	12	0	0	0	2	0	0	4	0	2	$A_{1g} + E_g + T_{2g} + T_{1u} + T_{2u}$
D_6^2	6	0	2	2	0	0	0	4	0	2	$A_{1g} + E_g + T_{1u}$
D_{24}^3	24	0	0	0	0	0	0	0	0	4	$A_{1g} + E_g + T_{1g} + 2T_{2g} + A_{2u} + E_u + 2T_{1u} + T_{2u}$
D_{12}^4	12	0	0	0	2	0	0	4	0	2	$A_{1g} + E_g + T_{2g} + T_{1u} + T_{2u}$
D_{24}^5	24	0	0	0	0	0	0	8	0	0	$A_{1g} + A_{2g} + 2E_g + T_{1g} + T_{2g} + 2T_{1u} + 2T_{2u}$
D_8^6	8	2	0	0	0	0	0	0	0	4	$A_{1g} + T_{2g} + A_{2u} + T_{1u}$

representations reduce in the case of rock-salt structure. The superscript 1, 2, . . . or 6 for the reducible representation D in the first column of the table stands for the first, second, . . . or sixth neighbour involved in the associated pair while the subscript represents the number of possible equivalent sets for the particular kind of associated pair. One can easily see that the irreducible representations for the pairs involving first, second, third, fourth, fifth and sixth nearest alkali vacancies in CsCl structure will be respectively the same as those for the pairs involving the second, first, sixth, second, fifth and third nearest neighbouring alkali vacancies in rock-salt structure.

It is possible that the divalent ions may form pairs with impurities like O^{--} . In such a case for rock-salt structure there will be six equivalent first nearest neighbour positions for O^{--} (in halogen sites) and the energy levels of such pairs will be sixfold degenerate and the corresponding irreducible representation will be $A_{1g} + E_g + T_{1u}$. For CsCl structure as there will be eight equivalent first nearest positions for O^{--} the corresponding irreducible representations will be $A_{1g} + T_{2g} + A_{2u} + T_{1u}$.

If there is a rapid hopping of the vacancies for the impurity defects in the equivalent positions one may expect, because of the different possible interactions in the system, a splitting of the energy levels as indicated by the different irreducible representations. Such a splitting being small will probably be observable in nuclear quadrupole resonance, or in Raman spectroscopy using sharp laser sources or probably in electron magnetic resonance.

This discussion will probably hold good also in systems in which magnetic pairs can be formed by two neighbouring spins.

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