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LETTER TO THE EDITOR

Ligand positions and crystal field parameters for Cr^{3+} at tetragonal sites in MgO

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Abstract. Ligand positions for Cr^{3+} at tetragonal sites in MgO are calculated from a lattice relaxation model. Using these ligand positions in conjunction with the parameters previously derived from the $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ system, we obtain the tetragonal crystal field parameters and the splittings of the low-lying energy levels for the present Cr^{3+} system. These results are compared with some experimental data and some fallacious calculations found in the literature are pointed out.

The tetragonally coordinated Cr^{3+} centre in MgO was first identified by Wertz and Auzins (1957) in analysing their EPR spectra and they proposed that the site is formed by a next-nearest-neighbour (002) cation vacancy. Subsequently, continuous interest has been directed at obtaining the low-lying level splittings of this tetragonal Cr^{3+} centre using other experimental methods (see, for example, McDonagh *et al* 1980) and the perturbation method (Macfarlane 1967, Fairbank and Klauminzer 1973). Furthermore, Du and Zhao (1986) have recently proposed a method for obtaining the positions of ligands coordinated to the Cr^{3+} ion in which the displacement ΔR of the oxygen ligand lying between the Cr^{3+} and vacancy was fitted (with an adjustable covalency parameter N as well) to the measured splittings of the Cr^{3+} ground state ${}^4\text{A}_2$ and first excited state ${}^2\text{E}$ and the other five ligands are held at perfect cubic positions. The fitting turned out to be very good (falsely) but was disputed by Zheng (1988) in the aspect that the result for the ${}^2\text{E}$ state is very sensitive to the ligand distance R_0 . Therefore, it would be of great interest to approach the present system in some different ways and to point out some errors found in previous approaches.

Firstly, the Yeung and Newman (1988) lattice relaxation model is employed to calculate the distorted ligand positions. In this model, the displacements and polarisation for every ion in the defect crystal are treated using the discrete atomistic basis and the equilibrium equations of ionic positions are decoupled into very small size matrix equations in the reciprocal-lattice space by Fourier transformations. Using the ligand positions calculated from this model, a satisfactory description of the spin-Hamiltonian parameters in terms of the superposition model has been achieved in several ionic systems such as the Eu^{2+} at orthorhombic sites in the alkali halides (Yeung and Newman 1988), the $3d^5$ ions Fe^{3+} and Mn^{2+} at cubic and non-cubic sites in some alkaline-earth oxides (Yeung 1988a) and some lanthanide ions, Eu^{2+} , Gd^{3+} and Tm^{2+} , at the cubic sites in fluorites (Yeung 1988b). In fact, the present system is isomorphous to the one with Fe^{3+} at tetragonal sites in MgO in which the ligand positions have been calculated

Table 1. Calculated ligand positions for Cr^{3+} at the tetragonal site in MgO with a nearby charge-compensating vacancy. (See Yeung (1988a), figure 1, for the detailed coordinate frame used.) There are four planar ligands (with $\varphi^\perp = 0^\circ, 90^\circ, 180^\circ$ or 270°) on the square-planar positions R^\perp and θ^\perp and the vacancy is lying above the ligand R^\parallel along the z axis.

Ligand coordinate	Value
<i>Planar</i>	
$\{R^\perp$ (Å)	1.9438
$\{\theta^\perp$ (deg)	94.02
<i>Axial</i>	
$\{R^\parallel$ (Å)	1.7720
$\{\theta^\parallel$ (deg)	0
$\{R^\perp$ (Å)	2.0277
$\{\theta^\perp$ (deg)	180

by Yeung (1988a). Hence, using the same set of force parameters for the MgO lattice, the Cr^{3+} ion is found to be displaced by 0.15 \AA towards the vacancy. Taking the Cr^{3+} as the origin and the z axis as pointing towards the vacancy gives the polar positions of the six coordinated oxygen ligands as shown in table 1. It is immediately apparent that the Du and Zhao model is oversimplified and their equivalent $R_1^\parallel = R_0 - \Delta R = 2.1 - 0.056 = 2.044 \text{ \AA}$ is much greater than our value.

Secondly, we shall predict (without fitting to any observed data for the present system) the values of the tetragonal crystal field parameters B'_{20} and B'_{40} for the distorted component of the crystal field potential $V_{\text{tetra}} = B'_{20}C_0^2 + B'_{40}C_0^4$ in addition to the dominant cubic one (with parameter Δ)

$$V_{\text{cubic}} = \frac{21}{10} \Delta [C_0^4 + \sqrt{\frac{5}{14}} (C_4^4 + C_{-4}^4)]$$

where C_q^k is the renormalised spherical harmonic function. The present B'_{20} and B'_{40} parameters are related to the conventional parameters μ and δ (Macfarlane 1967) by

$$\mu = -\frac{4}{7} B'_{20} - \frac{5}{21} B'_{40} \quad \delta = \frac{3}{7} B'_{20} - \frac{5}{21} B'_{40}.$$

Yeung and Newman (1986) made a successful superposition model analysis of the EPR parameters for the strain-induced ground state 4A_2 splittings of $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ and derived reliable sets of intrinsic crystal field parameters \bar{B}_k and t_k . Under the superposition model assumption, those parameters can be transferred to the present $\text{Cr}^{3+}:\text{MgO}$ system to provide values of the tetragonal crystal field parameters using the following superposition model formulae:

$$B'_{20} = \frac{1}{2} \bar{B}_2 \sum_i \left(\frac{\bar{R}}{R_i} \right)^{t_2} (3 \cos^2 \theta_i - 1)$$

$$B'_{40} = \frac{1}{8} \bar{B}_4 \sum_i \left(\frac{\bar{R}}{R_i} \right)^{t_4} (35 \cos^4 \theta_i - 30 \cos^2 \theta_i + 3) - \frac{1}{2} \bar{B}_4.$$

where $\bar{R} = 1.9085 \text{ \AA}$ is the mean ligand distance in the $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ system. The polar ligand positions $(R_i, \theta_i, \varphi_i)$ are taken from table 1 and used to obtain the values of B'_{k0} that

Table 2. Calculated tetragonal crystal field parameters and calculated splittings of some low-lying levels using the complete matrix diagonalisation for $\text{Cr}^{3+}:\text{MgO}$ with a nearby cation vacancy. All parameters and splittings are in cm^{-1} . See Fairbank and Klauminzer (1973) for level splitting labels and values of other parameters.

Parameter or splitting level	Fairbank and Klauminzer (1973)	Present work		Measured value
		Set A	Set B	
B'_{20}	4550	3885	4101	
B'_{40}	2520	2406	1787	
$\Delta E(^4A_2)$	0.145	0.135	0.112	0.164†
$\Delta E(^2_aE)$	87.1	94.1	98.7	93.5‡
$\Delta E(^2_aT_2)$	$\begin{cases} -182 \\ -183 \end{cases}$	$\begin{cases} -86 \\ -150 \end{cases}$	$\begin{cases} -136 \\ -171 \end{cases}$	$-133(\pm 60)\S$

† Wertz and Auzins (1957).

‡ McDonagh *et al* (1980).

§ Fairbank and Klauminzer (1973).

are given in table 2. The intrinsic parameters used in the sets A and B of calculations are respectively (Yeung and Newman 1986) $\bar{B}_2 = 3.97 \times 10^4 \text{ cm}^{-1}$, $t_2 = 1.24$, $\bar{B}_4 = 1.41 \times 10^4 \text{ cm}^{-1}$, $t_4 = 2.9$ and $\bar{B}_2 = 4.04 \times 10^4 \text{ cm}^{-1}$, $t_2 = 1.3$, $\bar{B}_4 = 1.17 \times 10^4 \text{ cm}^{-1}$, $t_4 = 3.4$. Making allowance for the variations in the input parameters, the calculated B'_{k0} are highly consistent with the values derived by Fairbank and Klauminzer (1973) directly from their experimental data. Further comparison with experimental data is made by evaluating the low-lying level splittings (zero if there is no non-cubic crystal field) through the diagonalisation of the complete Hamiltonian matrix which includes Racah's electrostatic parameters $B = 570 \text{ cm}^{-1}$ and $C = 3165 \text{ cm}^{-1}$, Tree's correction $\alpha = 70 \text{ cm}^{-1}$, the spin-orbit parameter $\zeta = 240 \text{ cm}^{-1}$, the cubic crystal field parameter $\Delta (= 10 Dq) = 16450 \text{ cm}^{-1}$ taken from Fairbank and Klauminzer (1973), and the tetragonal crystal field parameters B'_{k0} given in table 2. It is noted that the calculated (static contribution) ground state splitting $\Delta E(^4A_2)$ is always smaller than the measured value because there is the dynamical (lattice vibrational) contribution to the $\Delta E(^4A_2)$, which has been estimated by Manoogian (1979) to be about 6% of the static contribution. As shown in table 2, our calculated splittings for the excited states 2_aE and 2_aT_2 are somewhat closer to the measured values than those of Fairbank and Klauminzer. This verifies both the reliability of the calculated ligand positions (table 1) and the transferability of the superposition model parameters derived previously from the $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ system.

Thirdly, we tabulate in table 3 the calculated values of splittings for the 4A_2 and 2_aE states obtained using the parameters of Du and Zhao (1986) in which their best fitted ligand displacement $\Delta R = 0.059 \text{ \AA}$ and the covalency parameter $N = 0.95$. It must be noted that Du and Zhao's (1986) original perturbation results are fallacious as their given formulae do not lead to their published values and their values have been amended partially in their later reply (Du and Zhao 1988) to Zheng's (1988) comment. However, their amended result for $\Delta E(^2_aE)$ is not at all in agreement with the measured value, possibly due to a sign error in their formula for the parameter δ . With this correction, we recalculate the splittings using the corrected perturbation approach and the complete matrix diagonalisation approach. It is found that the values of $\Delta E(^2_aE)$ calculated using

Table 3. Calculated values of $\Delta E(^4A_2)$ and $\Delta E(^2E)$ in cm^{-1} for the tetragonal $\text{Cr}^{3+}:\text{MgO}$ system obtained using Du and Zhao's parameters with the covalency parameter $N = 0.95$ and fitted $\Delta R = 0.059 \text{ \AA}$.

Approach	$4\Delta E(^4A_2)$	$\Delta E(^2E)$
Du and Zhao (1986) (fallacious)	0.161	108
Du and Zhao (1988)	—	201
Corrected perturbation	0.067	157
Complete matrix diagonalisation	0.068	52
measurement†	0.164	93.5

† See table 2 for reference.

the perturbation approach and the complete matrix diagonalisation approach are very different. However, many people have overlooked the fact that the traditional second-order perturbation approach (Macfarlane 1967) for $\Delta E(^2E)$ is very inaccurate as the energy denominator for the nearby 4T_2 state ($\leq 1000 \text{ cm}^{-1}$) is smaller than the perturbation term, namely, the tetragonal crystal field with parameter B'_{k0} (or δ and μ).

Finally, we stress that distorted ligand positions should be calculated from the more reliable lattice relaxation model which includes all possible ligand displacements, not from Du and Zhao's approach which is too unrealistic. In fact, similar approaches suggested by Zhao and co-worker for other systems such as MnF_2 and ZnF_2 have been found to be at fault by Bauer and Sharma (1986). Moreover, we also emphasise that the perturbation approach with the formulae given by Macfarlane (1967) may be very unreliable for some Cr^{3+} systems and must be checked with the complete matrix diagonalisation results. The present approach should be very useful in studying many other similar Cr^{3+} centres in MgO such as the orthorhombic centres and other tetragonal centres with a monovalent cation (instead of a vacancy) as a charge compensator.

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