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Local-structure model of K^+ site in $KTaO_3$:Fe^{3+}

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We study a local-structure model suggested recently by Laguta *et al.* for the K^+ site in $KTaO_3$:Fr^{3+}. It is shown to be unreasonable for explaining the unusually large value of the EPR parameter D from calculations on D. A new assumption on the local structure is proposed.

In a ferroelectric crystal of the ABO_3 type having the perovskite structure, the cubic crystal field at the A site is much weaker than at the B site[1] and the impurities of the iron-group series normally substitute for the B ions because the ion radius at the A site is about twice that at the B site.[2] For example, the electron paramagnetic resonance (EPR) zero-field splitting parameter D due to impurities at the B site in ABO_3 has been measured in $SrTiO_3$,[2-5] $PbTiO_3$,[6-8] $BaTiO_3$,[8-10] and $KTaO_3$ (Refs. 11 and 12) doped with Mn^{2+} and Fe^{3+}. However, the parameter D at the A site was observed only in $KTaO_3$:Mn^{2+} (Ref. 13) and $KTaO_3$:Fe^{3+}.[12]

Siegel and Müller[14] have recently studied the EPR parameter D of Mn^{2+} on the K^+ sites in $KTaO_3$:Mn^{2+} on the K^+ sites in $KTaO_3$:Mn^{2+} and suggested an off-center position; i.e., all the oxygens remain in their cubic positions, whereas the center Mn^{2+} ion moves about 1–1.3 Å along the c axis when Mn^{2+} substitutes for K^+ (Fig. 1). Three years later, Bykov *et al.*[12] reported a very large value of $D=4.46\ \mathrm{cm}^{-1}$ in $KTaO_3$:Fe^{3+} and attributed it to Fe^{3+} on the K^+ site. The value is much greater than $D=1.33\ \mathrm{cm}^{-1}$ of Fe^{3+} on the Ta^{5+} site in the same lattice. However, one would expect a smaller value of D at the K^+, for there is a weaker crystal field.[1] To understand the unusually large value of D, Laguta *et al.*[15] recently made the following assumptions: (a) It gives rise to an excess positive charge in the lattice when an Fe^{3+} ion replaces K^+. This must be compensated by two electrons that can be provided by an O^{2-} ion located in the nearest interstice along the c axis. (b) Since the ionic radius of Fe^{3+} is approximately half that of K^+, the Fe^{3+} ion may move along the c axis and the resultant interstice can be occupied by an O^{2-} ion. In fact, the assumed local structure model is the off-center model proposed by Siegel and Müller[14] with an additional oxygen (hereafter O_{ad}) on the c axis. Afterwards this model was cited in some works.[16-19] Now we estimate this model by calculating the parameter D.

During the past few decades, two successful methods have been used to investigate the EPR parameters of d^5 (^6S) ion in crystals. One is by studying the various microscopic mechanisms which were supposed to have made contributions to the EPR parameters, and the other is the Newman superposition model[20-23] which involves dominant contributions of various microscopic mechanisms in a sense. Recently, a set of studies[24,25] for the spin-Hamiltonian parameters of d^5 ions showed that both methods are good approaches to accurate calculations and can lead to results almost identical with that from the d^5 ground-state splitting. The most important one of all microscopic mechanisms is the spin-orbit interaction, which has been studied in detail and applied successfully to rhombic and trigonal symmetries by Sharma and coworkers.[26-30] The axial EPR term D has been given as

$$D_{\mathrm{s.o.}}=\frac{\sqrt{2}}{12}\zeta^2\langle\gamma^4\rangle(2P_{\alpha\alpha}-P_{\alpha\beta})P_{\alpha\gamma}A_0^{4'}\ , \tag{1}$$

$$A_0^{4'}=-\tfrac{1}{8}\sum_i eQ_i(35\cos^4\theta_i-30\cos^2\theta_i+7\sin^4\theta_i\cos4\phi_i+3)/R_i^5\ , \tag{2}$$

where ζ is the spin-orbit coupling constant, Q_i and (R_i, θ_i, ϕ_i) the charge and coordinates of ith ligand, $P_{\alpha\alpha}$, $P_{\alpha\beta}$, and $P_{\alpha\gamma}$ the constants depending on the crystal-field strength.[26] Taking the values of $P_{\alpha\alpha}$, $P_{\alpha\beta}$, $P_{\alpha\gamma}$, ζ, and $\langle r^4\rangle$ to be the same as in MgO:Fe^{3+},[29,31] Eq. (1) is reduced to

$$D_{\mathrm{s.o.}}=-6.783\left[\frac{\text{Å}^5}{e^2}\right]A_0^{4'}\ . \tag{3}$$

From Eq. (2), the contribution to $A_0^{4'}$ from O_{ad} assumed by Laguta *et al.*[15] is obtained as $2e^2/R^5$ (where $Q=-2e$ for an O^{2-}). Since the sign of $2e^2/R^5$ is positive, it is easy to see from Eq. (3) that the contribution from O_{ad} decreases $D_{\mathrm{s.o.}}$ rather than increases it. For comparison, two sets of $D_{\mathrm{s.o.}}$ for the cases (with and without O_{ad}) are listed in Table I. In the calculation for the case with O_{ad}, the distance R(Fe-O_{ad}) is taken to be 2 Å for ionic radii $O^{2-}=1.32$ Å and $Fe^{3+}=0.64$ Å.[32]

We can also examine the model by means of the superposition model, which expresses the axial term D as

$$D_{\mathrm{SM}}=\tfrac{1}{2}\sum_i\bar{b}_2(3\cos^2\theta_i-1)\left[\frac{R_0}{R_i}\right]^{t_2}\ , \tag{4}$$

TABLE I. The comparison of calculated parameter D between the cases with and without additional oxygen O_{ad} (in cm^{-1}).

	I(without O_{ad})	II(with O_{ad})	$(D_{\mathrm{I}}-D_{\mathrm{II}})/D_{\mathrm{I}}$
$D_{\mathrm{s.o.}}$	0.792	0.368	54%
D_{SM}	0.656	0.316	52%
Expt.		4.46 (Ref. 12)	

where the intrinsic parameter $\bar{b}_2$ is negative in this case.[14,23,33] Because $\theta=\pi$ and thus $3\cos^2\theta-1=2$ for O_{ad}, the contribution to D_{SM} from O_{ad} is negative, which is contrary to the experimental observation. This qualitatively shows that the model seems unreasonable for explaining the EPR D. Two sets of D_{SM} are listed in Table I if the $\bar{b}_2/D$ and the t_2 are taken as Siegel and Müller did on the K^+ site in $KTaO_3$:Mn^{2+}.

From Table I, it is easily seen that the contribution from O_{ad} calculated by both the microscopic mechanism and the superposition model decreases the value of D to less than 50%. This shows that the attempt to explain the unusually large value of D by adding oxygen into the c axis failed for both methods of the microscopic mechanism and the superposition model, and, furthermore, the local structure model of the K^+ site in $KTaO_3$:Fe^{3+} proposed by Laguta *et al.*[15] is unreasonable for explaining the EPR parameter D.

Let's discuss this model further. The presence of the additional oxygen O_{ad} on the c axis seems reasonable for compensating the charge and unreasonable for explaining the EPR D. Therefore, we assume (assumption I) that the charge compensation is remote as the situations in $LiNbO_3$:Fe^{3+} (Ref. 34) and $LiTaO_3$:Fe^{3+},[35] i.e., the distance R(Fe-O_{ad}) is large enough [for example, R(Fe-O_{ad}) > 3 Å, i.e., O_{ad} is close to the O_9-O_{12} plane in Fig. 1]. In this case the contribution from O_{ad} is negligibly small for $D_{s.o.}\propto 1/R^5$, $D_{SM}\propto 1/R^8$. This is consistent with the result given by Siegel and Müller,[14] that the contributions to D from O_9-O_{12} are very small. If the "assumed" additional oxygen is excluded in the calculation, the discrepancy between the calculated and the measured values of D is most probably because of the rough assumption that all the oxygens remain in their original positions when Fe^{3+} ions are substituted. Since the ionic radius of Fe^{3+} is smaller than that of Mn^{2+} and much smaller than that of K^+,[32] the surrounding oxygens may move as they do in other situations.[36-44] If the displacement to the center, caused by the difference of ion radius and charge between Fe^{3+} and K^+, is in an irregular way, we have to treat many free parameters (R_i, θ_i, ϕ_i) and therefore are not able to establish a useful model of local structure. Therefore, we assume (assumption II) that all nearest-neighbor oxygens O_1-O_8 move towards the c axis in their original planes (Fig. 1) as the behavior of the oxygens shown by Siegel and Müller[14] on the Ta^{5+} site in $KTaO_3$:Fe^{3+}. In this case the coordinates (R_i, θ_i, ϕ_i) for nearest neighbors are determined only by the size of the movement. We find that fitting the observed $D=4.46$ cm^{-1} requires the size of the movement to be about 0.3 Å. The local relaxation is significant and reasonable for the large difference of the ionic radius of Fe^{3+}(0.64 Å) and K^+ (1.32 Å),[32] though it needs further support from other methods.

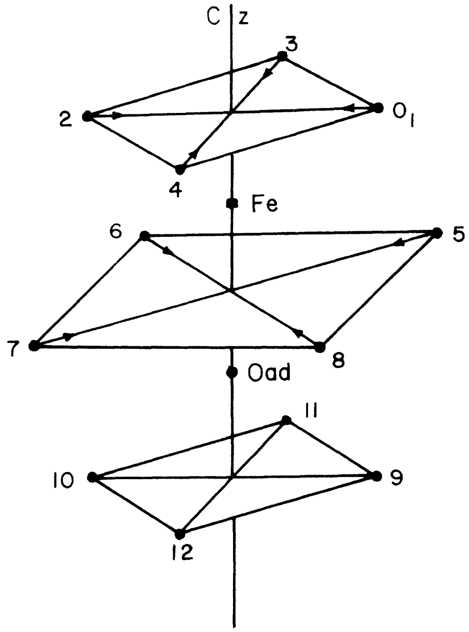

FIG. 1. Local environment of an off-center Fe^{3+} at K^+ site in $KTaO_3$. The position of O_{ad} is assumed approximately by Laguta *et al.* (Ref. 15). Arrow (→) represents the direction of displacement of oxygen ion assumed in this paper.

In short, the unusually large value of zero-field splitting parameter D in $KTaO_3$:Fe^{3+} is not explained by nearby charge compensation about the center ion Fe^{3+} but well fitted by the modified model described by using assumptions I and II (in brief, a local relaxation about the center ion Fe^{3+}), even though its actual structure is not quite clear as yet.

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