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Comments

Comments are short papers which criticize or correct papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Local structure of the axial Fe^{3+} center in the K^+ site of a $KTaO_3$ crystal

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In order to understand the unusually large value of zero-field splitting D for the axial Fe^{3+} center in a $KTaO_3$ crystal, Zhou made two assumptions in his recent report [Phys. Rev. B **42**, 917 (1990)]. In this Comment we will show that his assumption II is qualitatively reasonable, whereas assumption I is unnecessary and doubtful.

To understand the unusually large value of the EPR parameter $D(=4.46\ \mathrm{cm}^{-1}$, Ref.1) for the axial Fe^{3+} center in a $KTaO_3$ crystal, Laguta *et al.*[2] suggested that this center represents an Fe^{3+} ion at the K^+ site. 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 additional O^{2-} (hereafter O_{ad}) for providing charge compensation. Recently, by approximately calculating the parameter D from the spin-orbit-coupling mechanism[3] and the superposition model,[4] Zhou[5] found that the contribution from O_{ad} decreases D rather than increases it and hence thought that although the presence of O_{ad} in the vicinity of Fe^{3+} is reasonable for compensating the charge, it is unreasonable for explaining the EPR D. On this basis, he made two assumptions: (I) The compensator O_{ad} is remote, i.e., the distance $R(\text{Fe-O}_{ad})$ is large enough so that the contribution to D from O_{ad} is negligibly small and cannot decrease the large observed value of D. (II) The eight nearest-neighbor oxygens atoms O_1-O_8 move towards the c axis in their original planes. This local relaxation causes a large tetragonal distortion and crystal field and hence a large EPR D. For assumption II, it is qualitatively reasonable because the Fe^{3+} carries heavier charge than K^+ and has a stronger attraction for the oxygen ions. For assumption I, however, the reasons given in Ref. 5 are not sufficient and not satisfactory. The following points are, in our opinion, obviously unfavorable to this assumption.

(1) According to Zhou's calculation,[5] when the O_{ad} is in the vicinity of Fe^{3+}, the contribution from O_{ad} is $-0.424\ \mathrm{cm}^{-1}$ from the spin-orbit-coupling mechanism, which is too small when compared with the observed value of D. So, the large D is mainly due to the contribution from O_1-O_8. The O_{ad}, whether it is close to Fe^{3+} or not, is of no importance. Thus, the assumption that O_{ad} should be remote from Fe^{3+} because its contribution decreases D is unsatisfactory. In fact, since so large a contribution to D ($4.46-0.792=3.668\ \mathrm{cm}^{-1}$) can be obtained by assuming that the O_1-O_8 move towards the c axis about 0.3 Å in their original planes, as shown in Ref. 5, why not assume that O_1-O_8 move slightly further so that the contribution from the additional displacement (except 0.3 Å) can cancel that from O_{ad}. In passing, the fitting procedure was not clearly given in Ref. 5, so the additional displacement cannot be estimated quantitatively. If Eqs. (2), (3), or (4) given in Ref. 5 are used, one can find that the displacement (0.3 Å) in Ref. 5 is not sufficient for fitting such a large D (note: the calculated D from the displacement 0.3 Å and the equations given by Zhou[5] are about $1/3-1/2$ of the observed $D=4.46\ \mathrm{cm}^{-1}$). So, Zhou's quantitative estimates are doubtful. Considering that the large decrease of $R(\text{Fe—O}_{1-8})$ due to the displacement will increase not only $1/R^5$, but also $\langle r^4\rangle$ (due to electron-cloud expansion[6]) and $(2P_{\alpha\alpha}-P_{\alpha\beta})P_{\alpha\gamma}$ (due to the stronger crystal field[7]), the free parameters should be more than those (R_i,θ_i,ϕ_i) in Ref. 5. So the quantitative estimate of the displacement by fitting EPR D, even though it is rough, is impractical. So, the calculation in Ref. 5 cannot repel the presence of O_{ad} in the vicinity of Fe^{3+}. Assumption I is unnecessary.

(2) Although many investigations[8,9] show that if a small impurity ion substitutes for a larger ion in a cubic ionic crystal, the induced electric dipoles together with the decreased repulsive forces could indeed cause the impurity to be located at an off-center site; however, in some cases, such as Co^{2+} and Mn^{2+} in $SrCl_2$ crystals[10,11] (for ionic radius, 0.72 and 0.80 compared with 1.12 Å, Ref. 12), this phenomenon does not occur, but the potential energy well of impurity becomes flatter.[13] Because the above "off-center" systems are related to the delicate balance of the various contributions to the potential energy such as the Coulomb interaction, polarization, and repulsive interaction in the substances, the determination of which one being "on-center" or "off-center" is

difficult. For Fe^{3+} in a K^+ site of a $KTaO_3$ crystal, the cubic center has been observed from EPR measurement,[14] suggesting that the on-center site of Fe^{3+} replacing K^+ is stable (although the potential well along the c axis may be flatter). Particularly, when an electric field of $E \sim 150$ KV/cm was applied no changes were observed in the EPR spectrum of this cubic center.[15] This further supports the suggestion. Note that when comparing with the case of Mn^{2+} in $KTaO_3$, Siegel and Muller[16] pointed out that since the ionic radius of Fe^{3+} is less than that of Mn^{2+}, it would be astonishing if Mn^{2+} were on an off-center position and Fe^{3+} were not. So, the difference of ionic radius is not the only cause for the appearance of an off-center impurity, and other reasons should be given. In our opinion, the presence of O_{ad} due to charge compensation is perhaps an important one. Because the charge of O_{ad} is opposite to that of Fe^{3+}, the Coulomb interaction should make them close to each other. It may be the approaching of O_{ad} towards the Fe^{3+} ion that leads to the large repulsive force that pushes the Fe^{3+} into the off-center site. It appears that O_{ad} cannot be remote from the Fe^{3+} ion. More importantly, as pointed out by Laguta *et al.*[2], the annealing experiments support strongly the above suggestion. The increase in the number of the off-center due to annealing in oxygen shows that the axial Fe^{3+} center results from the O_{ad}. A subsequent helium annealing decreases the number of off-center Fe^{3+} ions, suggesting that the excess oxygen ions, i.e., O_{ad} are displaced from the lattice and the charge compensation occurs in coordination spheres more distant from the Fe^{3+} ion and the symmetry of the center becomes cubic. In addition, annealing in water vapor reduces the concentration of axial centers and increases that of cubic centers; this can be explained reasonably by assuming that the charge compensation is provided by the OH^- which is located in the more distant coordination spheres because of its high mobility and so the axial center becomes cubic. Thus, from the exchange of off-center with on-center ions in various annealing atmospheres, one can come to the opinion that O_{ad} is remote from Fe^{3+} in the on-center (cubic) system, whereas in the off-center (axial) system, it is not. So, if from point (1), assumption I in Ref. 5 is unnecessary, then, from point (2), this assumption is unreasonable.

In conclusion, assumption II in Ref. 5 is qualitatively reasonable, even though the quantitative estimate is doubtful, whereas assumption I is, in our opinion, unnecessary and unreasonable.

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