COMMENTS

Comment on “Local Lattice Structure Study of the Octahedral $(CrO_6)^{9-}$ Clusters for Cr^{3+} Ion Doping in a Variety of Oxide Crystals by Simulating the Corresponding EPR and Optical Spectra”

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The microscopic origin of optical and magnetic properties displayed by Cr^{3+} impurities in oxide lattices is a subject of current interest as it plays a key role for understanding the color exhibited by gemstones like ruby (Al_2O_3:Cr^{3+}), emerald ($Be_3Si_6Al_2O_{18}$:Cr^{3+}) or alexandrite ($BeAl_2O_4$:Cr^{3+}). In a recent paper Kuang et al. claim[1] that reasonable values of the mean equilibrium $Cr^{3+}-O^{2-}$ distance, R (and also of the small distortion undergone by the oxygen octahedron), can be obtained from an analysis of experimental values of optical transitions and EPR parameters through a parametrized crystal-field model. In essence such an analysis is founded on two main assumptions: (1) Electronic properties due to Cr^{3+} impurities in oxides can be understood considering *only* the $CrO_6{}^{9-}$ complex at the right equilibrium geometry. (2) Accordingly, changes in the cubic field splitting parameter, 10 Dq, reflect necessarily variations of R following the law $10\ Dq = KR^{-n}$, where K is a constant and the exponent n would be close to 5.

As the color of insulating oxides doped with Cr^{3+} essentially depends on the energy of the first spin allowed ${}^4A_{2g}$ $(t_{2g}{}^3) \rightarrow$ ${}^4T_{2g}$ $(t_{2g}{}^2e_g)$ transition,[2] which is just equal to 10 Dq, such assumptions mean that a change in color implies a variation of the average equilibrium $Cr^{3+}-O^{2-}$ distance. By virtue of this fact in the analysis carried out by Kuang et al. the experimental 10 Dq values measured for emerald (16130 cm^{-1}) and ruby (18070 cm^{-1}) are explained by stating[1] that mean equilibrium $Cr^{3+}-O^{2-}$ distances are $R = 202$ and 195.4 pm for emerald and ruby, respectively. However, this conclusion is against experimental EXAFS data,[3−5] which unambiguously prove that emerald and ruby have the same R value (equal to 197 pm) within the experimental uncertainty (1 pm). Along this line a nearly equal value $R = 198 \pm 1$ pm has recently been measured[6] for the spinel $MgAl_2O_4$:Cr^{3+}. It is certainly surprising that these relevant experimental facts are not taken into consideration in the paper[1] by Kuang et al. In fact, information on the actual R values for ruby and emerald is given in refs 3 and 7, which are also quoted in the paper[1] by Kuang et al.

From a fundamental point of view the wrong conclusion reached by Kuang et al. is thus not different from that reached by Orgel 50 years ago.[8] This author already showed that, in the framework of the traditional ligand field theory, the different color displayed by ruby and emerald can only be explained by assuming that R(emerald) − R(ruby) should be around 5 pm.

It has recently been shown that this failure of the traditional ligand field theory obeys the fact that properties of a transition metal impurity, M, in an insulating lattice are assumed to be explained only through the MX_N complex (formed with the N ligands) in vacuo.[7,9] However, although active electrons are usually confined in the complex region they are *also* subject to the internal electric field, $\mathbf{E}_R$, due to all ions of the insulating host lattice lying outside the complex. Accordingly, 10 Dq also depends on the shape of $\mathbf{E}_R$ in the complex region and not only on the actual R value. Interestingly, the effects of the internal electric field, $\mathbf{E}_R$, have been shown to be not necessarily negligible even if the host lattice is cubic.[9] In the case of Cr^{3+} impurities in oxides the validity of this idea has been proved[7,10] through ab initio calculations carried out on a $CrO_6{}^{9-}$ complex at the right equilibrium geometry and subject to the corresponding $\mathbf{E}_R$ field. The shape of this internal field in the complex region is strongly dependent on the type of host lattice. By means of this procedure (where no parameters are employed) the different color exhibited by ruby, emerald and the two centers formed in the alexandrite has been explained in a reasonable way,[7,10] thus without invoking different R values for ruby and emerald, a fact not consistent with recent experimental findings.[3−5]

References and Notes

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