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Ravi Sekhar, Y.; Bill, Hans

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EPR studies on an "unperturbed" CrO_4^{3-} center in K_2SO_4 crystals

Y. Ravi Sekhar and H. Bill
Groupe de Physico-Chimie du Solide, Université de Genève, 30, Quai E. Ansermet, 1211 Geneva 4, Switzerland

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Electron paramagnetic resonance of CrO_4^{2-} doped K_2SO crystals has been studied after x-irradiation at 77 K. The resulting species, a CrO_4^{3-} center, has the principal g values $g_x = 1.8743$, $g_y = 1.8507$, and $g_z = 1.9386$. The EPR data indicate a small distortion of CrO_4^{3-} tetrahedra. A temperature variation study of the spectra in the range 1.6–77 K shows that they broaden rapidly above 10 K and no motionally averaged spectrum is observed. The experimental results are discussed in terms of several effects including a possible Jahn–Teller effect.

The nature of the ground state and electronic structure of CrO_4^{3-} and MnO_4^{2-} ions have attracted considerable attention in recent years.[1] The unpaired electron responsible for the EPR in these clusters was found to occupy a d_{z^2} or d_{xy} ground state depending on the lattice and the distortion of the host XO_4^{n-} ion from ideal T_d symmetry.[2-5] In our previous investigations,[6] we have attempted to study and compare CrO_4^{3-} and MnO_4^{2-} ions in the same lattice (namely K_2SO_4) in order to obtain a consistent basis to establish the electronic structure in their ground state. The crystals of CrO_4^{2-} doped K_2SO_4 were x irradiated at 300 K to produce CrO_4^{3-} ions and their EPR was studied. It turned out that the results obtained on the CrO_4^{3-} were quite different (with respect to the g values, and their orientation) from those obtained in MnO_4^{2-} doped K_2SO_4 crystals.[2] This different behavior was attributed to the presence of a nearby proton (produced by RT irradiation) as evidenced by ENDOR measurements.[6] In the present paper, we report on a CrO_4^{3-} center which does not seem to have any nearby lattice defect or impurity associated. We have succeeded in creating this center by irradiating the crystals at 77 K.

Single crystals of K_2SO_4:CrO_4^{2-} have been grown by slow evaporation of aqueous solutions. The presence of the CrO_4^{2-} impurity has been checked by optical and Raman spectroscopies. The unpolarized Raman lines were observed at $\nu_1(A_1)$: 865 cm^{-1}, $\nu_2(E)$: 354 cm^{-1}, $\nu_3(T_2)$: 390, 394, 399 cm^{-1}, and $\nu_4(T_2)$: 900, 906, 925 cm^{-1}. The as-grown crystals did not show any EPR lines. They were then irradiated at 77 K using a Philips x-ray generator at 40 kV and 40 mA for about 24 h. No new EPR lines associated with CrO_4^{3-} were found at 77 K while well defined resonances could be seen at 4.2 K. A temperature variation study showed that these EPR lines broaden rapidly above 10 K and were not detectable above about 18 K.

Figure 1 shows the experimental spectra along the c axis. The hyperfine lines from the 9.5% abundant ^{53}Cr ($I = 3/2$) are clearly seen only along this direction. The low field lines at $g = 2.0423$ and $g = 2.0094$ in Fig. 1 are readily identified as due to SO_4^- and SO_3^- radicals respectively, resulting from the damage of the host SO_4^{2-} ions.[6] The angular variation of the g values has been studied in the three crystallographic planes and are depicted in Fig. 2. When the magnetic field is rotated in an (a, b) or (a, c) plane, a single line is seen while in the (b, c) plane (the mirror plane of the crystal), two lines appear except along the b and c axes. K_2SO_4 crystals belong to the orthorhombic space group D_{2h}^{16} (at RT) with four sulphate ions per unit cell.[7] These four ions can be divided into two pairs where members of a pair are related by reflection in the (a, b) and (a, c) planes. The SO_4^{2-} ions in the K_2SO_4 lattice occupy sites of C_s symmetry. The observed angular dependence of the spectra agrees with a C_s site symmetry of the CrO_4^{3-} ion. Note that CrO_4^{3-} ion has one unpaired electron ($S = 1/2$).

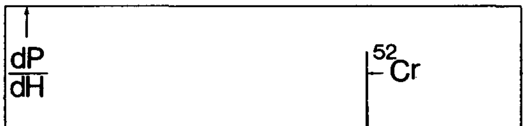

FIG. 1. X-band EPR spectrum of CrO_4^{2-} doped K_2SO_4 crystals along c axis at 4.2 K after x irradiation at 77 K. The ^{53}Cr hyperfine components are indicated by the stick diagram below.

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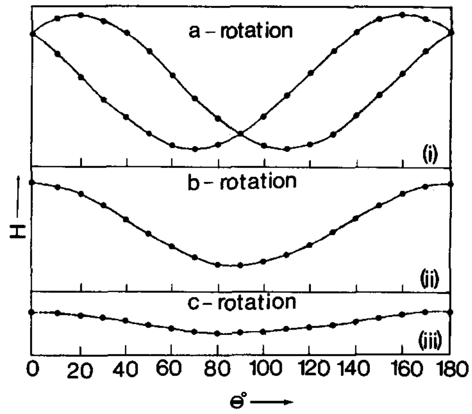

FIG. 2. The angular variation in the three crystallographic planes of the line at $g = 1.9289$ in Fig. 1. (i) (b, c) plane (with b axis at $\Theta = 0°$); (ii) (a, c) plane (with a axis at $\Theta = 0°$); (iii) (a, b) plane (with b axis at $\theta = 0°$).

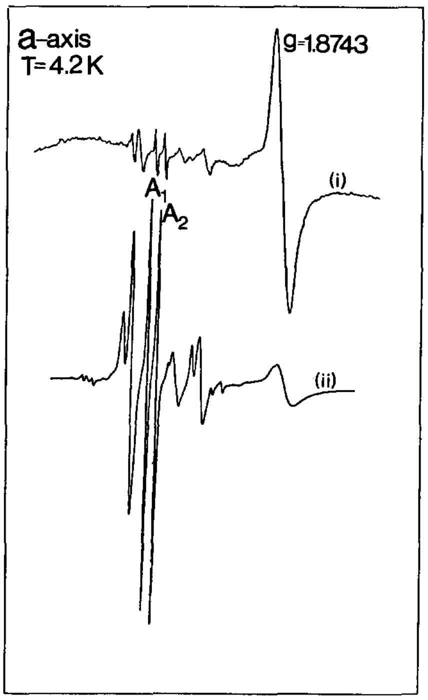

FIG. 3. Comparison of the two CrO_4^{3-} centers produced in $K_2SO_4{:}CrO_4^{2-}$ crystals. The EPR spectra shown are taken along the a axis under identical conditions. (i) Spectrum at 4.2 K after x irradiation at 77 K identified as due to CrO_4^{3-} without any associated defect. (ii) Spectrum at 4.2 K after irradiation at 300 K. The lines marked as A_1 and A_2 have been discussed earlier in Ref. 6 and identified as due to CrO_4^{3-} with a nearby proton.

Experimentally, we have the following situation: when the crystals are irradiated at 300 K, the main species of the damage is the CrO_4^{3-} center with a nearby proton. The CrO_4^{3-} center without any associated defect is also produced under these conditions but with a much lower yield. On the other hand, when the crystals are irradiated at 77 K, the presently reported CrO_4^{3-} centers seem to form more efficiently than those associated with protons. We have indeed observed comparable concentrations of these two different centers in a number of crystals. Figure 3 summarizes these observations.

The principal g values of the presently reported CrO_4^{3-} center are given in Table I along with the earlier data on relevant systems. The C_s symmetry of the molecule requires that one of the principal g values, designated as g_x here, is along the a axis (direction perpendicular to the mirror plane). The other two, g_y and g_z, lie in the mirror plane (b, c). We can now compare our results with those obtained on MnO_4^{2-} in K_2SO_4 and K_2CrO_4 crystals earlier.[2,8] In order to unify the different results, the orientation of the g tensor in the mirror plane is represented geometrically in Fig. 4 in each of these cases. Note that the EPR experiments do not allow us to distinguish between the two possible orientations of the g tensor in the mirror plane (g_y, g_z and $g_{y'}$, $g_{z'}$). However, we notice from Table I and Fig. 4 that CrO_4^{3-} in K_2SO_4 has a predominantly d_{z^2} ground state as $(g_e - g_x), (g_e - g_y) > (g_e - g_z)$ where $g_e = 2.0023$.

The ^{53}Cr hyperfine lines could be resolved at only a few orientations owing to (i) the angular dependent line widths and (ii) the presence of weak lines from other centers. As can be seen from Fig. 1 and Fig. 3, the main EPR line has a width of about 4 G along c axis ($g = 1.9289$) and broadens up to about 28 G along other orientations. These facts coupled with the low intensity of the ^{53}Cr EPR lines precluded us from making a complete analysis of the hyperfine data. However, from the plots of $A^2g^2 = A^2g^2[\cos^2(\theta - \theta_0)]$, an approximate estimation of the principal A values was obtained. These are $A_x = 36$, $A_y = 30$, and $A_z = 8 \times 10^{-4}\ \mathrm{cm}^{-1}$ and $\theta_0 \simeq 25°$. Here, A_x is parallel to the a axis of the crystal and A_y, A_z are oriented in the bc plane. The noncoincidence of the g and A tensors has been observed in many of the CrO_4^{3-} and MnO_4^{2-} doped systems studied earlier[6] and is associated with the molecular nature of these centers. A comparison of the present results with those obtained in CrO_4^{3-} doped Li_3PO_4 crystals[3] shows that A_x, A_y, and A_z are in the same order of magnitude in the two cases. It may be remarked that the hyperfine structure data in the latter case are also complicated by the line broadening and no consistent fitting could be achieved. Thus, these data remain very tentative in view of the uncertainty in the measurements.

TABLE I. Principal g values of $CrO_4{}^{3-}$ and $MnO_4{}^{2-}$ ions in different hosts.

System	g_x	g_y	g_z	Approximate ground state	Ref.
$K_2SO_4 : CrO_4{}^{3-}$	1.8743	1.8507	1.9386	d_{z^2}	Present work
$Li_3PO_4 : CrO_4{}^{3-}$	1.7411	1.7722	1.9402	d_{z^2}	3
$K_2SO_4 : MnO_4{}^{2-}$	1.9696	1.9757	1.9445	d_{xy}	2
$K_2CrO_4 : MnO_4{}^{2-}$	1.970	1.966	1.938	d_{xy}	8

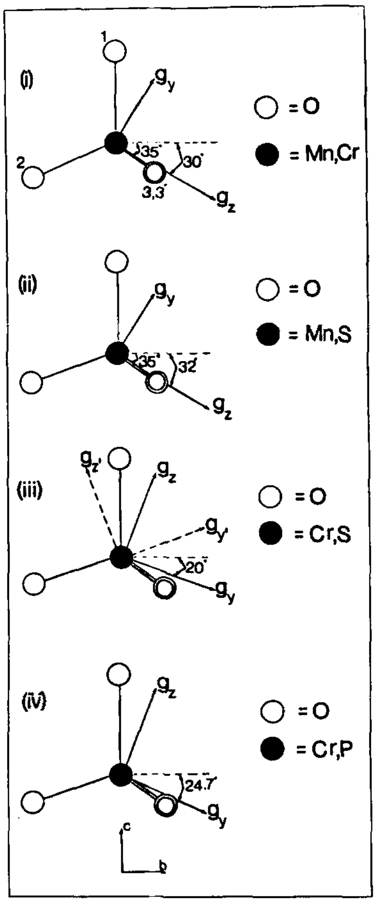

FIG. 4. Orientation of the principal g values in the mirror plane in various cases: (i) MnO_4^{2-} doped K_2CrO_4; (ii) MnO_4^{2-} doped K_2SO_4; (iii) CrO_4^{3-} produced in K_2SO_4 by irradiation at 77 K. g_y, g_z and $g_{y'}$, $g_{z'}$ indicate here the two possible orientations. (iv) CrO_4^{3-} doped Li_3PO_4.

Another interesting feature of the present system is that it exhibits no motionally averaged spectrum. Again, this is a clear indication that the ground state wave function of the CrO_4^{3-} is of molecular nature. Indeed, within a pure $3d$ E-type orbital picture, the spin-orbit coupling has no matrix elements which are essential for the electron dephasing.[10]

The fact that it is not possible to decide experimentally between the two orientations of g in the (b, c) plane leads to some ambiguity in the theoretical interpretation of the data. Both the solutions, shown in Fig. 4, however do not seem to support the predominance of a trigonal or a tetragonal component in this low symmetry system. From Table I and Fig. 4, we notice that the present CrO_4^{3-} center in K_2SO_4 has similar characteristics to the analogous center in Li_3PO_4 crystals[3] as regards the g values, their order and orientation in the mirror plane. Another common feature is the temperature dependence. Both exhibit EPR only below about 25 K. The CRO_4^{3-} introduced into Li_3PO_4 host also has particularly large Δg values. Li_3PO_4 is a remarkable host in the sense that the PO_4^{3-} ions are very nearly tetrahedral,[9] although it belongs to the same space group as K_2SO_4 crystals. The comparison between our results and those obtained in Li_3PO_4 seems to us quite valuable. It shows that an adequate description of the ground state of XO_4^{n-} centers has to involve a consideration of several effects which are probably in a rather delicate mutual balance. Indeed, there is a possibility of a $E \otimes \epsilon$ (tetragonal) type molecular Jahn–Teller effect,[10] or a trigonal $E \otimes \epsilon$ molecular JT effect, together with the low symmetry lattice ligand field. It is well known, based on the angular overlap model,[11] that tetrahedral (tetragonal) $E \otimes \epsilon\ d^1$ systems imply rather small JT coupling constants whereas the trigonal JT effect involves stronger ones. But, this latter effect goes through an admixture of excited states (via the trigonal part essentially of the intramolecular ligand field) which transform as T_2 in tetrahedral symmetry. In addition, the intermolecular ligand field in these hosts is not very strong as is shown by the short relaxation times. Thus, it is likely that all the three effects discussed above are to be considered simultaneously (eventually in part in the form of a pseudo-Jahn–Teller effect), because a straightforward application of the crystal field model leads to quite inconsistent conclusions. This fact is supported by the noncoincident orientations of g and ^{53}A indicating important s, p oxygen contribution to the ground state wave function of the molecular ion.

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