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# EPR of $Cr^{3+}$ in Tris(acetylacetonato)gallium(III) Single Crystals

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EPR of $Cr^{3+}$ in gallium acetylacetonate was studied at X-band. Two crystallographically inequivalent centers were observed. Their spin-Hamiltonian parameters ($g = 1.997$ (3); $|b_2^0| = 0.593$ (3) and 0.599 (3) $cm^{-1}$, respectively; $|b_2^2| = 0.03$ (7) and 0.09 (7) $cm^{-1}$, respectively) differ very little from each other and from those for the isomorphous aluminum and cobalt(III) compounds. No changes were observed between 298 and 20 K. Thus, the geometry of the paramagnetic ion in such molecular crystals seems to be little affected by changes in the size of the host ion and temperature. The zero-field-splitting (ZFS) pattern can be satisfactorily reproduced by the superposition model with an intrinsic ZFS parameter $|\overline{b_2}|$ of 5.0 $cm^{-1}$. This pattern thus seems to be largely caused by the distortion of the first coordination sphere of oxygens. The cause of occurrence of two crystallographically inequivalent centers could not be determined.

In previous EPR studies of $Cr^{3+}$ in the isomorphous acetylacetonates of Al(III) and Co(III) almost identical results were obtained for both compounds.[1,2] The effects of a phase transition in the aluminum compound were also studied.[3] A tripling of the unit cell with three very similar centers of $Cr^{3+}$ was found below the phase transition temperature; their EPR parameters differed only slightly from those at room temperature. Despite the triclinic point symmetry of the trivalent metal ions, the spectra were found to be almost axial with the pseudo triad axes of the complexes coinciding with the magnetic $z$ axes of the zero-field-splitting (ZFS) tensor. It thus appears that the geometry of the chromium ion in these molecular crystals is rather insensitive to changes in the size of the host ion and temperature.

$Ga(acac)_3$ is also isomorphous with the corresponding Al, Co, and Cr compounds,[4] which crystallize in the monoclinic space group $P2_1/c$ with four formula units in the unit cell. A crystal structure refinement for the gallium compound is also available.[5] This compound is therefore suitable for a further test of the insensitivity of the EPR parameters of $Cr^{3+}$ to changes in the size of the host ion and temperature.

Single crystals of $Ga(acac)_3$ were grown by slow evaporation from acetone solutions at room temperature with 1-3 mol % of the chromium compound added to the solutions. Crystals containing between 0.5 and 1 mol % Cr were studied by EPR at X-band between 298 and 20 K. As shown in Figure 1, two crystallographically inequivalent, but very similar, centers of $Cr^{3+}$ were found. They split further into pairs of magnetically inequivalent sets symmetric to the $b$ axis, as expected for the reported point and space groups. The data were analyzed by using the spin-Hamiltonian

$$\mathcal{H} = \beta HgS + b_2^0\left[S_z{}^2 - \frac{1}{3}S(S + 1)\right] + \frac{b_2^2}{3}(S_x{}^2 - S_y{}^2)$$

appropriate for orthorhombic or lower point symmetry. The numerical results are listed in Table I together with those for the Al and Co compounds from the literature. As shown in the perspective view in Figure 2, the $z$ axes for the Ga compound are in the $b$-$c$ plane +29 and +26° from $b$ whereas the $y$ axis is obtained by clockwise rotation of the $-a$ axis around $z$ by +37 and +49°, respectively. Thus the orientations of the principal axes are also very similar to those reported for the other two compounds.[1-3] The values for the axial splitting parameters $|b_2^0|$ of 0.593 and 0.599 $cm^{-1}$ agree reasonably well with that obtained from the ZFS's of 0.8-1.0 $cm^{-1}$ observed in the luminescence spectra.[6]

**Table I.** EPR Parameters of $Cr^{3+}$ in Acetylacetonates

| host ion | temp/K | | $g$ factor | $\lvert b_2^0\rvert/cm^{-1}$ | $\lvert b_2^2\rvert/cm^{-1}$ | ref |
|---|---|---|---|---|---|---|
| Al | 298 | | 1.983 (2) | 0.592 (2) | 0.156 (6) | 1 |
| | 295 | | 1.985-1.997 | 0.597 | 0.081 | 3 |
| | 110 | A | 1.983-1.987 | 0.600 | 0.0125 | 3 |
| | | B | 1.987-1.992 | 0.587 | 0.0155 | 3 |
| | | C | 1.978-1.985 | 0.591 | 0.0148 | 3 |
| Co | 298 | | 1.9802 (5) | 0.600 (1) | 0.0255 (15) | 2 |
| Ga | 20-298 | A | 1.997 (3) | 0.593 (3) | 0.03 (7) | this work |
| | | B | 1.997 (3) | 0.599 (3) | 0.09 (7) | this work |

A closer inspection of Figure 1 reveals that up to four closely spaced signals were observed instead of the two arising from the two centers with slightly different EPR parameters. They evidently consist of pairs of these two centers differing in orientation by a rotation of about 3° around the $a$ axis. The origin of this additional doubling is still obscure. Twinning of the crystal would result in additional doubling, but normally such twins differ in orientation by much more than 3°.

Within the limits of error quoted in Table I, no changes were observed between 298 and 20 K. Thus, unlike the Al and Co compounds, the Ga compound exhibits no phase transition in this temperature range.

Assuming the ZFS to be solely due to the distortion of the first coordination sphere of oxygens, the experimental ZFS pattern can be compared with that calculated from the crystal structure data for the pure host compound. Alternatively, the crystal structure data for the pure chromium compound[8] could be used for this comparison. However, due to the very similar lattice parameters the geometries are not very different, and thus effects of local lattice relaxation around the chromium impurity ions can also be expected to be small. The superposition model (SPM) of Newman and Urban[7] allows such a detailed comparison, both qualitatively (i.e., for the orientations of the principal axes of the ZFS parameters) and quantitatively (i.e., for the signs and sizes of the distortions obtained along different directions). It can be written as

$$b_2^m = \sum_i K_2^m(\theta_i,\varphi_i)\left(\frac{R_0}{R_i}\right)^{t_2}\cdot\overline{b_2}$$

with $m = 0$ or 2, $K_2^m$ the coordination factors, and $\theta_i$ and $\varphi_i$ the angles between the M-$X_i$ vectors and the $z$ and $x$ axes, respectively.

Although validity of the SPM is by no means established experimentally for $Cr^{3+}$ in contrast to the S-state ions $Mn^{2+}$ and $Fe^{3+}$, it was applied to this ion in uniaxial stress experiments and the exponent $t_2 = -0.2$ and the intrinsic ZFS parameter $|\overline{b_2}| =$

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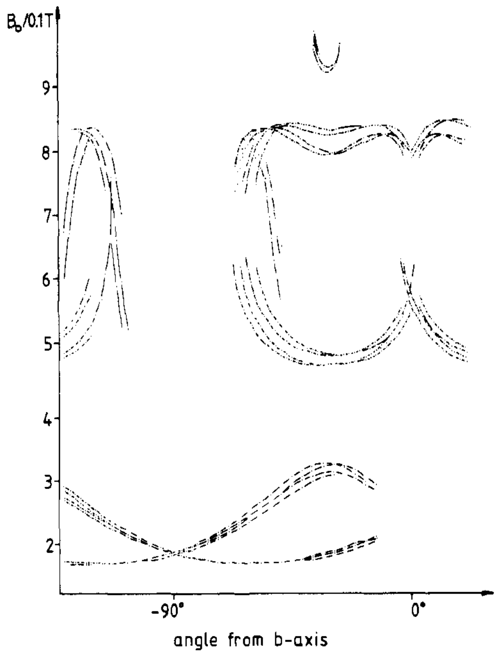

**Figure 1.** Angular variation of the EPR signals of $Cr^{3+}$ in tris(acetylacetonato)gallium(III) for rotation around the crystallographic *a* axis at 9.56 GHz and room temperature. No change in line positions was observed with cooling to 20 K.

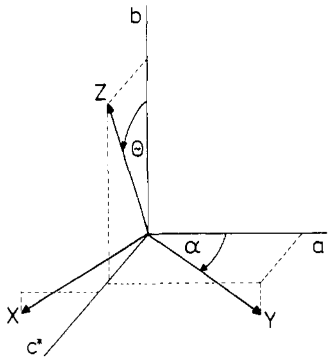

**Figure 2.** Perspective view of the orientations of the principal axes for $Cr^{3+}$ in $Ga(acac)_3$ relative to the crystal axes *a*, *b*, and *c**.

1.95 $cm^{-1}$ were determined for MgO as host lattice.[10] The actual exponent $t_2$ is of little influence in our case due to the very similar sizes of $Ga^{3+}$ and $Cr^{3+}$ and bond length differences of at most 1%. As shown in Figure 3, the experimental ZFS pattern in the $z$–$y$ plane can be reproduced very satisfactorily by the crystal structure data for the pure gallium compound with the exponent $t_2 = 6$ (in analogy to the case of $Fe^{3+}$)[9] and an intrinsic ZFS parameter (i.e., the ZFS per unit distortion $|\bar{b}_2| = 5.0$ $cm^{-1}$. It is significantly larger than the value obtained in uniaxial stress experiments and still larger than those obtained for other (purely inorganic) compounds with oxygen coordination,[11] perhaps due to the $\pi$-electron system of the acetylacetonate ligands. Although for $Cr^{3+}$ in general and for such complicated ligands in particular validity of the SPM is by no means certain, it appears that indeed in this case the ZFS pattern is largely determined by distortion of the first coordination sphere.

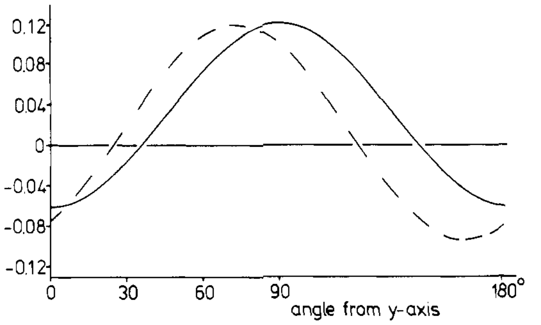

**Figure 3.** Comparison of the experimental ZFS pattern in the magnetic $z$–$y$ plane with that calculated from the crystal structure data of the host compound. The full curve is the experimental ZFS divided by $2\bar{b}_2$ ("splitting diagram").[12] The dashed curve is given by the following expression, where $\theta_i$ are the angles between the Ga–$O_i$ vectors and the

$$\tfrac{1}{2}\sum_i (3\cos^2\theta_i - 1)(R_0/R_i)^6$$

particular direction and the summation runs over the six oxygens ("distortion diagram").[12] The numbers on the ordinate thus denote distortions in terms of "effective fractional ligand at normal bond distance".

The very similar ZFS splitting patterns for this ion in all three acetylacetonates seem to indicate that for molecular crystals of more complicated ligands the surrounding of the impurity ion is very similar to that for the pure transition-metal compound and is thus very little affected by the size of the host ion. This contrasts strongly with inorganic structures for which considerable variations of the ZFS parameters are observed in isomorphous compounds, and discrepancies between experimental and calculated ZFS patterns in cases of size mismatch between host and impurity ion strongly indicate variable, but sometimes very strong, effects of local lattice relaxation.[11] The sensitivity of the EPR parameters against changes in the size of the host ion and temperature should also be tested for high-spin $Fe^{3+}$ and $Mn^{2+}$ in such molecular type structures since for these S-state ions a large body of experimental evidence has been accumulated showing that the ZFS patterns indeed closely reflect the geometries of their first coordination spheres in systems for which effects of local lattice relaxation can be expected to be small.

The origin of the two crystallographically inequivalent centers with slightly different EPR parameters in the Ga compound is still obscure. Simultaneous presence of $\alpha$ and $\beta$ modifications[4] could be the cause, but varying ratios of the two spectra would be expected in different samples whereas in fact equal intensities were always observed within the limits of error. Inspection of the crystals under the polarizing microscope also gave no indication of the presence of two phases. Likewise, the cause for occurrence of two sets of spectra with a difference in orientation of only 3° could not be determined.

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**Registry No.** $Cr^{3+}$, 16065-83-1; $Ga(acac)_3$, 14405-43-7.

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