Quadrupole interaction of the SrTiO$_3$:V^{4+} system

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Analysis were made to calculate the quadrupole interaction of the Jahn-Teller SrTiO$_3$ system from enhanced EPR spectra due to an applied static electric field. The calculations gave a value for the quadrupole constant
$|P| = (-2.142\ 0.005)\times10^{-4}$ cm^{-1}.

EPR spectra of vanadium doped SrTiO$_3$ crystals were reported before [1,2]. The spectra stemmed from a V^{4+} (d^1) $S = \frac{1}{2}$ ion substituted for Ti^{4+}. It was concluded that the SrTiO$_3$:V$^+$ impurity was a strong Jahn-Teller ion which resulted in a compression of the oxygen octahedron. Later, static electric field experiments in EPR confirmed this conclusion [2,3]. The static electric field gives rise to an appreciable lowering of the dielectric constant of SrTiO$_3$, especially at low temperatures [4,5] leading to a better quality factor Q of the resonant cavity. The quality factor Q expresses the ratio between its energy loss per period [6]. Therefore this leads to a much better sensitivity of the EPR measurements and this resulted in observing small satellite lines stemming from 'forbidden' quadrupole transitions (see figure). Therefore we were able to calculate the quadrupole constant.

As said before in the electric field experiments we observe in EPR not only an enhancement of the EPR lines, which stem from centres with tetragonal axes parallel to the applied electric field, but also new small lines in the [100] direction (see figure).

The quadrupole term for the spin Hamiltonian is equal to (see also reference [7]):

$$\mathcal{H} = \boldsymbol{I}.\boldsymbol{P}.\boldsymbol{I}, \tag{1}$$

where $\boldsymbol{P}$ is the quadrupole coupling tensor.
In the principal axis system Eq.1 can be written as:

$$\mathcal{H} = P_{xx}I_x^2 + P_{yy}I_y^2 + P_{zz}I_z^2 \tag{2}$$

In the case of axial symmetry the quadrupole coupling tensor is traceless so the Hamiltonian becomes:

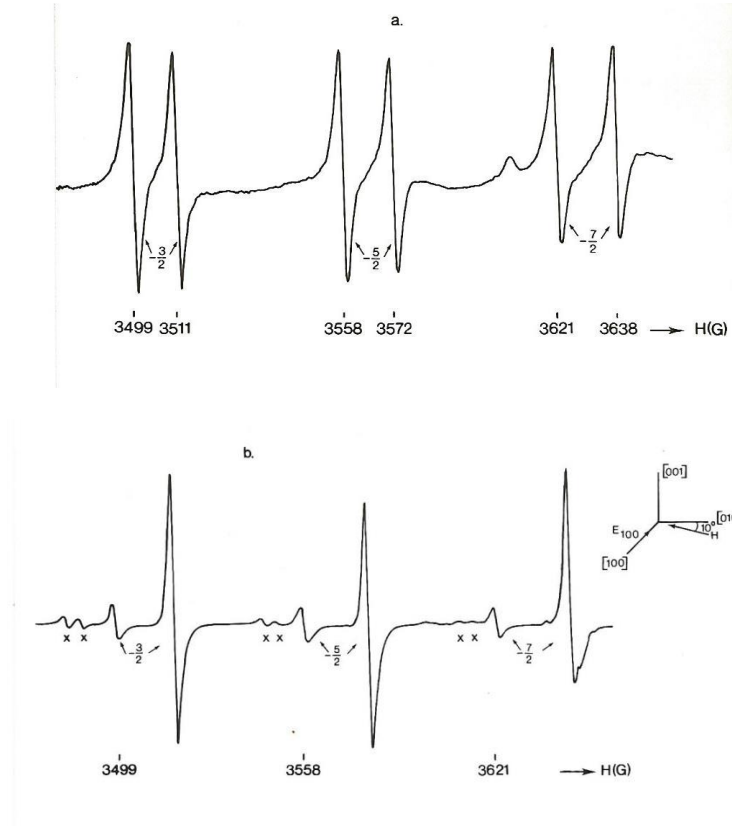$$\mathcal{H} = P\{I_z^2 - \tfrac{1}{3}I(I+1)\} \tag{3}$$

$$P = \tfrac{3}{2}P_{zz}$$

Figure. (a) EPR spectrum of the SrTiO$_3$:V^{4+} system for $\boldsymbol{H}$ in the (001) plane, about 10° away from the [010] axis, T = 4.2 K. (b) The same spectrum, but with an applied field $\boldsymbol{E}$ ∥ [100], E = 21 kV cm^{-1}. The lines marked × are 'forbidden' quadrupole transitions. (figure taken from references [3] and [2].

Assuming that the principal axis of the quadrupole coupling tensor coincide with those of the g and hyperfine tensors we obtain:

$$\mathcal{H} = \frac{P}{2}\left\{\left(\frac{3A_\parallel^2 g_\parallel^2}{g^2 A^2}\right)cos^2\theta - 1\right\}\{I_z^2 - \frac{1}{3}I(I+1)\} - \frac{P}{2}\left(\frac{A_\parallel A_\perp g_\parallel g_\perp}{g^2 A^2}\right)sin2\theta\{I_z I_x + I_x I_z\} +$$

$$+\frac{P}{4}\left(\frac{A_\perp^2 g_\perp^2}{g^2 A^2}\right)sin^2\theta\{I_x^2 - I_y^2\}, \tag{4}$$

where $gA = (A_\parallel^2 g_\parallel^2 cos^2\theta + A_\perp^2 g_\perp^2 sin^2\theta)^{1/2}$.

The first term gives a first order contribution to the energy of the state $|M_S M_I\rangle$ and shifts the energy states connected by $\Delta M_I = 0$ equally. The second and third term mix respectively states $|M_S, M_I \pm 1\rangle$ and $|M_S, M_I \pm 2\rangle$ with $|M_S, M_I\rangle$. Because these terms are mixed, transitions of $\Delta M_I = \pm 1$ and $\Delta M_I = \pm 2$ become weakly allowed.

At $\theta = 0°$ the $\Delta M_I = \pm 1$ and $\Delta M_I = \pm 2$ transitions have zero intensity, while at $\theta = 90°$ the $\Delta M_I = \pm 1$ lines have zero intensity and the $\Delta M_I = \pm 2$ lines have intensity. In the V^{4+}:$SrTiO_3$ system we expect 12 possible transitions.

The energy differences for these $\Delta M_I = \pm 2$ transitions are:

$$E\left(+\tfrac{1}{2}, M_I \pm 1\right) - \left(-\tfrac{1}{2}, M_I \mp 1\right) = h\upsilon = g\mu_B + AM_I \pm 4P_\theta M_I \mp 2G_I, \tag{5}$$

where $P_\theta = \frac{P}{2}\left\{\left(\frac{3A_\parallel^2 g_\parallel^2}{g^2 A^2}\right)\cos^2\theta - 1\right\}$ and $G_I = \frac{g_N^{(I)} \mu_B^{(I)} H}{gA}(A_\parallel^2 g_\parallel^2 \cos^2\theta + A_\perp^2 g_\perp^2 \sin^2\theta)$

At $\theta = 90°$, P_θ in Eq. 5 becomes $-\frac{P}{2}$

From the position of the small quadrupole lines at $\theta = 90°$ (with the magnetic field $\vec{H}$ parallel to the [100] direction) and with the help of Eq. 5, we calculated that
$|P| = (-2.142 \pm 0.005)\times 10^{-4}$ cm^{-1}.
This value is in the same order of magnitude as those values found for V^{4+} in GeO_2 [8] and TiO_2 [9], respectively.

One very important assumption was made: There is no change in $|P|$ by changing the magnitude of the electric field. Because there was no change in hyperfine interaction on changing the magnitude of the electric field, we think that our assumption is right.

References

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