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HAL Id: jpa-00209411
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Submitted on 1 Jan 1982

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Magneto-optical properties of the excited state of F-centres in some alkali-halides: addendum

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(Reçu le 23 juin 1981, accepté le 29 septembre 1981)

Résumé. — Le facteur de Landé orbital et la structure spin-orbite du premier état excité des centres F dans KF, RbCl et RbBr sont mesurés; ces résultats expérimentaux et ceux d'autres auteurs sont comparés aux valeurs théoriques calculées par Harker.

Abstract. — The orbital \( g \)-factor and the spin-orbit splitting of the first excited state of F-centres are measured in KF, RbCl and RbBr crystals. Our experimental results and others are compared with Harker’s theoretical values.

In a previous paper [1] we mentioned the relative scarcity of experimental data to check Harker’s calculations [2] of magneto-optical parameters of the alkali-halides F-centres; this addendum presents results of measurements about orbital \( g \)-factor (\( g_{\text{orb}} \)) and spin-orbit splitting (\( \Delta \)) of the first unrelaxed excited state in KF, RbCl and RbBr crystals.

We used samples of various origins (Cornell University, Harshaw, Laboratoire de Physique cristalline of Paris XI University); they are coloured by \( ^{60}\text{Co} \gamma \)-irradiation. As previously described [1] we observe the F-band absorption and magnetic circular dichroism, as a function of temperature (1.5-1.6 K, 90-105 K and 190-200 K); the experimental data are analysed by Henry et al.’s moments method [3], and uncertainties from various origins are estimated [1]. The experiments are performed with two samples of each crystal and three or four measurements are made in each temperature range on each of the samples.

Tables I and II show \( \Delta \) and \( g_{\text{orb}} \) respectively: we compare our experimental results (second column) with other published results (*) (third column) and with Harker’s theoretical values (last columns).

The large uncertainty of \( g_{\text{orb}} \) in RbBr results from a huge «paramagnetic correction» even at high temperature (> 90 K), because of the large value of \( \Delta \).

These new experimental results together with those of reference [1], confirm that \( g_{\text{orb}} \) tends to increase with cation size, as Harker’s calculations [2] predict; in other words, our three new values, when plotted on figure 1c of [1] make it look more like the theoretical curves 1a and b. The behaviour with the anion seems much less systematic.

We now have at our disposal reliable experimental data concerning ten alkali-halides (LiF, KF, NaCl, KCl, RbCl, NaBr, KBr, RbBr, KI and RbI); and are thus able to check the reliability of the theoretical calculation of an observable \( q \), through the quantity

\[
\Delta q = \frac{1}{\sqrt{n}} \sum_{i=1}^{n} \left( \frac{q_{\text{th}} - q_{\text{ex.}}}{q_{\text{ex.}}} \right)^2 (n = 10)
\]

where \( q_{\text{th.}} \) and \( q_{\text{ex.}} \) are respectively the computed and measured values of \( q \). In table III we compare the \( \Delta q \) values with a mean estimate of the experimental precision, for the transition energy (\( \varepsilon \)), \( \Delta \) and \( g_{\text{orb}} \). It appears that the ion-size correction much improves the theoretical values of \( \varepsilon \), but unfortunately tends to increase the \( \Delta \) and \( g_{\text{orb}} \) discrepancies. Anyhow, the \( \Delta q \) are clearly larger than the experimental precisions.

We are currently investigating with A. H. Harker if these discrepancies are due to:
- unjustified assumptions in the F-centre model...
Table I. — *Spin-orbit splittings* : $\Delta$ (in meV).

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Observed</th>
<th>Calculated $^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>this work</td>
<td>other works</td>
</tr>
<tr>
<td>KF</td>
<td>5.68 ± 0.34</td>
<td>5.0 ± 0.9</td>
</tr>
<tr>
<td>RbCl</td>
<td>19.3 ± 1.1</td>
<td>15.1</td>
</tr>
<tr>
<td>RbBr</td>
<td>29.2 ± 1.4</td>
<td></td>
</tr>
</tbody>
</table>

Table II. — *Orbital g-factors* : $g_{\text{orb}}$.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Observed</th>
<th>Calculated $^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>this work</td>
<td>other works</td>
</tr>
<tr>
<td>KF</td>
<td>0.79 ± 0.08</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>RbCl</td>
<td>0.96 ± 0.15</td>
<td>0.74</td>
</tr>
<tr>
<td>RbBr</td>
<td>1.1 ± 0.4</td>
<td></td>
</tr>
</tbody>
</table>

Table III. — *Relative discrepancy between experimental and theoretical values* : $\Delta q$. $^e$ experimental values from W. B. Fowler, *Physics of Color Centers*, Academic Press, 1968; $g_{\text{orb}}$ and $\Delta$ experimental values from this work, [1], and its references.

<table>
<thead>
<tr>
<th>$q$</th>
<th>$\Delta q$</th>
<th>Experimental precision</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Point-ion</td>
<td>Ion-size</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>12.0%</td>
<td>44%</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>11.0%</td>
<td>15.0%</td>
</tr>
<tr>
<td>$g_{\text{orb}}$</td>
<td>19.5%</td>
<td>26.0%</td>
</tr>
</tbody>
</table>

(as for example, by neglecting the lattice distortions in the F-centre vicinity, the unspherical potential terms, the ion polarization or the exchange effects between the F and ion electrons...);
— unjustified approximations in $\Delta$ and $g_{\text{orb}}$ calculations (neglected terms, insufficient number of ions taken into account, ...).

Current work [10] shows that $g_{\text{orb}}$ results from three contributions, of which two are much larger than $g_{\text{orb}}$ but with opposite signs (see, for instance, relations (16) of [7] or (2.20) of [2]). Thus $g_{\text{orb}}$ is very sensitive to various approximations in calculations and to assumptions in the model. Particularly, we note:

* the important effect of the tails of electronic orbitals (F electron and ion-electrons) and consequently the crucial choice of the orbitals and the noticeable effect of terms involving orbitals, centred on different ions;
* the importance of the number of ions taken into account and of their positions.

Acknowledgements. — We particularly thank M. F. Bloquel, who made available for us a $^{60}$Co source of the Centre Régional François-Baclesse de Lutte Contre le Cancer de Caen.

References