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LANTHANIDE Z CENTERS IN ALKALI HALIDES

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Résumé. — Des résultats d’absorption et d’émission des centres Z₁, Z₂, Z₄ et Z₆ dans KC1 dopé aux terres rares Eu⁺⁺ et Yb⁺⁺ sont présentés et comparés avec ceux des centres Z(Sr) dans le même cristal. Le centre Z₂ et son modèle atomique sont discutés en détail en utilisant aussi les résultats des expériences EPR et ENDOR du centre Z₂(Eu) dans quelques halogénures alcalins.

Abstract. — Absorption and emission data of lanthanide Z₁, Z₂, Z₄ and Z₆ centers in KC1 are presented and compared with those of the Z(Sr) centers in the same host. Especially the Z₂ center and its configurational model is discussed in detail, using also the ESR and ENDOR data of Z₂(Eu) in various alkali halides.

In alkali halides containing Eu⁺⁺ or Yb⁺⁺ as impurities Z centers can be formed from F centers by roughly the same optical and thermal conversion processes as in the case of the alkaline earth dopants Sr⁺⁺ or Ca⁺⁺. Analogies and differences are best explained at the schematic drawings of figure 1, where the Z center formation processes are compared in europium, ytterbium and strontium doped KC1.

Up to now five different types of Z centers are known [1]. In a crystal rapidly quenched from 330 °C an almost pure F center system is present in all three examples. Irradiation with F-light at ~20 °C results in a complete conversion into Z₁ centers. Also the rare earth Z₁ absorptions are independent of the kind of the divalent impurity and found to lie at ~2.08 eV. The corresponding emissions are symmetrical gaussian bands: their peak positions and half widths are given in Table I and compared with the emission of the Z₁(Sr) center.

With higher initial F center concentrations also Z₄ centers are formed by the same conversion process. For all impurities in question the Z₄ absorption appears at about 1.43 eV at the low energy side of the M band. Emission bands which we ascribe to this center are again simple bell-shaped, but remarkably narrow (Table I). This behavior suggests a comparison to the M center (Eᵥ = 1.17 eV, Wᵥ = 0.19 eV). Similar to the case of the M center the Z₄ emissions can also be excited at higher energies in absorption bands probably hidden under the F absorption.

Annealing for several hours at 80 °C in the dark destroys the Z₁ centers in all these cases and leads to a formation of Z₂ and furtheron of F centers. Only in strontium-doped KC1 also a decomposition into Z₂ centers is registered.

In KC1 : Sr and KC1 : Eu there seems to exist some sort of thermal equilibrium between F and Z₂ centers: Z₂ centers can be formed at ~83 °C purely thermally. In KC1 : Yb this equilibrium is drastically shifted towards the side of the F center. A good conversion into Z₂ centers is accomplished in all these systems by an additional F irradiation. With ytterbium and strontium impurities a simultaneous Z₅ center formation cannot be avoided. Prolonged F irradiation of several hours finally destroys Z₂ centers in favour of Z₅ centers. The very best Z₅ center systems are found in crystals simply annealed in the dark at room temperature for several months.

Whereas the Z₅ center absorption is clearly separable only with the strontium impurity the emission bands for all three dopants are easily detectable (Table I). They are in form and half width comparable to the F center emission band. Magneto-optical experiments reveal, that the Z₅ center is also paramagnetic with the same sign as the F center.

The Z₅(Sr) center in KC1 shows no peculiarities from the view-point of simple absorption and emission spectroscopy, apart from the unusually long life time of 15 ms [2]. Our spectral data show some difference to the current literature and are therefore included in Table I.

In contrast to this the absorptions (Fig. 2) and emissions (Fig. 3) of the lanthanide Z₂ centers seem to be more complicated. At least 4 absorption bands for Z₂(Eu) and 2 absorptions for Z₂(Yb) can be separated out by computer simulation (Table I). The relation of the small absorption band at 1.98 eV to the Z₂(Eu) center is not assured. Optical excitation in the other absorption bands leads with various quantum efficiencies to two emission bands, called Z₂¹ and Z₂² (Fig. 3). The computer simulations and decompositions of the emission curves of figure 3 are performed with the data of about thirty experiments, where crystals with different concentrations...
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**FIG. 1.** — Schematic representation of the $Z$ center formation processes in KCl: Eu, KCl: Yb and KCl: Sr, as deduced from absorption and emission experiments.

of the participating centers and spectrally different excitations were used. It is seen that the $Z_2$ emissions are always accompanied by some $F$, $Z_4$ or $Z_5$ emission bands. With both impurities, europium and ytterbium, the $Z_2^{(1)}$ emission is connected with a long living excited state comparable to that which has been found for the strontium emission in KCl. The $Z_3^{(1)}$ emission is fast and recalls the situation of the fast $Z_2^{(1)}$ (Sr) emission recently found in NaCl [3]. These conclusions are simply drawn from the phase conditions at the lock-in detector used in our experiments. Direct measurements of the lifetimes and theoretical explanations of the various energy splittings are still outstanding.

More information about the $Z_2^{(1)}$ (Eu) center especially

**TABLE I**

<table>
<thead>
<tr>
<th>Crystal Peak/width (eV)</th>
<th>KCl : Eu</th>
<th>KCl : Yb</th>
<th>KCl : Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_d/W_d$</td>
<td>$E_b/W_b$</td>
<td>$E_d/W_d$</td>
</tr>
<tr>
<td>$Z_1$</td>
<td>2.08/0.285</td>
<td>0.955/0.335</td>
<td>2.09/0.314</td>
</tr>
<tr>
<td>$Z_2$</td>
<td>1.86/0.190</td>
<td>0.895/0.105</td>
<td>2.05/0.286</td>
</tr>
<tr>
<td>(1.98/0.120)</td>
<td>0.823/0.119</td>
<td>2.34/0.315</td>
<td>1.145/0.131</td>
</tr>
<tr>
<td>$Z_3$</td>
<td>2.12/0.194</td>
<td>2.37/0.367</td>
<td></td>
</tr>
<tr>
<td>$Z_4$</td>
<td>1.43/ —</td>
<td>0.707/0.103</td>
<td>1.43/ —</td>
</tr>
<tr>
<td>$Z_5$</td>
<td>— / —</td>
<td>1.055/0.281</td>
<td>— / —</td>
</tr>
</tbody>
</table>

**FIG. 2.** — Absorption spectra of $Z_2^{(1)}$ (Eu) and $Z_3^{(1)}$ (Yb) centers in KCl at liquid nitrogen temperature. The relation of the small band at 1.98 eV to the $Z_2^{(1)}$ (Eu) center is not assured.
which contains only the usual Zeeman term and the axially symmetric quadrupole part of the crystal field [4], [5]. Consequently the Z, (Eu) center possesses a <100> axial symmetry in all the above mentioned crystals. This is consistent with the earlier reported triplet resonance experiments on the conventional alkaline earth Z2 centers in various alkali halides [6]. The measured b_2^0 parameters are listed together with the g-factors and hyperfine constants in table II.

Table II

g-factors, axial quadrupole parameters b_2^0 and hyperfine constants for Z_2(Eu) centers in various alkali halides at liquid nitrogen temperature.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>g</th>
<th>b_2^0</th>
<th>A^151</th>
<th>A^153</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>1.994</td>
<td>1.890</td>
<td>-15.2</td>
<td>-6.6</td>
</tr>
<tr>
<td>KBr</td>
<td>1.991</td>
<td>1.880</td>
<td>-16.05</td>
<td>-6.7</td>
</tr>
<tr>
<td>RbCl</td>
<td>1.990</td>
<td>1.560</td>
<td>-14.4</td>
<td>-</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.998</td>
<td>2.380</td>
<td>-21.9</td>
<td>-10.2</td>
</tr>
<tr>
<td></td>
<td>±0.002</td>
<td>±5</td>
<td>±0.5</td>
<td>±0.5</td>
</tr>
</tbody>
</table>

The fitting of the ESR spectra with only this one crystal field parameter b_2^0 is best demonstrated by the Zeeman diagrams of figure 5. The 8S_7/2 ground state of the Eu^2+ ion is split by the crystal field into four Kramers doublets (H_z = 0). The transitions at the K band frequency of 24.23 GHz are indicated by small arrows. The calculations have been done for four angles \( \beta \) between the magnetic field direction \( H_z \) and the [001] direction of the crystal. A good agreement with the measured angular dependence is found. The lines shown in the spectrum of figure 4 appear in the Zeeman diagrams for \( \beta = 0 \) (||) and \( \beta = 90^\circ \) (\( \perp \)).

The conclusions drawn from the results of the experiments are best explained at a structure model as shown in figure 6. The resonance data confirm that there is only one divalent impurity incorporated in the Z2 center. From the absence of a paramagnetic resonance signal and of a temperature dependent magneto-optical effect in the conventional alkaline earth systems it is known, that there are two antiparallel electrons in the ground state. These may be located at one (model I) or at two separate anion vacancies (model II). Several years ago Ohkura [7] proposed the «perturbed F-model» (I) on the basis of some optical experiments: we would like to prefer a «2 F-model» (II). Both configurations possess a strict <100> axial symmetry.

From a comparison of the Z_2 center hyperfine constants A (Table II) with those of the neutral europium atom it can be concluded that 64% of the two F electrons in the Z_2 center or 1.28 electron charge are concentrated on the divalent europium ion, thereby reducing it about Eu^{2+}0.7. Also this is consistent with both models.
FIG. 4. — Electron spin resonance spectrum of the $Z_2$(Eu) center in KBr at liquid nitrogen temperature with the static magnetic field $H_z$ parallel to the [001] crystal direction. The designations are explained in the text.

FIG. 5. — Zeeman diagrams for the ground state of the $Z_2$(Eu) center in KBr calculated with only one crystal field parameter $b_4^2 = + 1.745 \times 10^{-4}$ cm$^{-1}$ (room temperature) for different angles between the static field $H_z$ and the [001] crystal direction. The measured lines are indicated by small arrows, those for $\beta = 0$ and $\beta = 90^\circ$ appear in the spectrum of figure 4.

FIG. 6. — Configurational models for the $Z_2$(Eu) center. Model I is called the « F'-model » (Ohkura), model II the « 2F-model » of the $Z_2$ center. Configurations III$\beta$ and II$\alpha$ may be related to $Z_2$ centers with other divalent impurity ions.
But ENDOR experiments on \(Z_2(Eu)\) in KCl, which can only briefly be mentioned because of lack of space, seem to support the 2F-model too:

i) the two chlorine ions neighbouring the \(Eu^{++}\) on the center axis are missing;

ii) there is only one \(K^+\) nucleus on the center axis in the fourth shell around \(Eu^{++}\);

iii) the measured isotropic superhyperfine constants of the nuclei in the 1st and the 2nd shell around \(Eu^{++}\), are of comparable magnitude. In model IIa these nuclei are all nearest neighbors to the molecule-type center.

If one believes such a 2F-model for the \(Z_2\) center, it has anyway to be kept in mind that it is proposed for the \(Z_2(Eu)\) center especially. In view of the different formation processes of the alkaline earth \(Z_2\) centers it must be stated, that model I is by no means ruled out for these impurities.

Nevertheless model II offers still further configurations with the cation vacancy at position \(\beta\) or \(\gamma\) depending on the binding energy of the impurity complex in various alkali halides. Therewith the missing [100] axial symmetry of the \(Z_2(Sr)\) center in NaCl as found in the triplet resonance experiments [6] may be explained.

References

[1] The \(Z_2\) center, which is assumed to be an ionized \(Z_2\) center, shall not be considered here.


DISCUSSION

A. B. Lidiard. — Have you accurate data on the thermodynamic equilibrium between \(F\) and \(Z_2\)-centres?

J. H. Paus. — We have not yet carried out detailed experiments on the reaction kinetics. This shall be done in the next future. Concerning the \(F-Z_2\) equilibrium I suspect that perhaps one of the two paramagnetic centers \(Z_1\) or \(Z_2\) may play some role in the \(Z_2\) formation process.

F. Luty. — The optical behavior due to triplet states should be markedly different for a one-vacancy and two-vacancy model, binding two electrons (\(F'\) and \(M\) type model), because in the former one the 1s triplet state is excluded by Pauli principle, for the latter one it is existent. Have you detected in the \(Z_2\) systems you described any triplet emission or absorption effects, similar to the ones of the Munich group? Their triplet results, in my opinion, clearly support a one-vacancy model.

J. H. Paus. — Up to now we have only observed an emission coming out of a long living excited state. As I said, direct measurements of this lifetime are not yet made. Triplet resonance experiments on the \(Z_2(Eu)\)-centers have been tried, but were not successful. The difficulties for the detection of such triplet resonances in the presence of the numerous \(Z_2(Eu)\) resonance lines are considerable.