The excited state of Z2 and Z+2 centres

H. Paus, W. Scheu

To cite this version:


HAL Id: jpa-00220069
https://hal.archives-ouvertes.fr/jpa-00220069
Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
The excited state of $Z_2$ and $Z_2^+$ centres

H. J. Paus and W. Scheu

Physikalisches Institut, Teil 2, Universität Stuttgart, Pfaffenwaldring 57 (7000) Stuttgart-80, W-Germany

Résumé. — Les spectres magnéto-optiques des centres $Z_2^+(Ca)$ et $Z_2^+(Yb)$ dans KCl montrent une structure surprenante, qui est expliquée par un caractère partiel d de l’état excité. L’effet spin-orbite de $Z_2^+(Ca)$ est négatif, de $Z_2^+(Yb)$ positif, ceci indique néanmoins une ressemblance frappante avec les centres F et $F_A$.

Abstract. — Magnetooptic spectra of $Z_2^+(Ca)$ and $Z_2^+(Yb)$ centres in KCl exhibit a surprising structure explained by a partial d-character of the excited state. The spin orbit effect of $Z_2^+(Ca)$ is negative, that of $Z_2^+(Yb)$ positive; this indicates nevertheless a close relation of these centres to F and $F_A$ centres.

1. Introduction. — EPR experiments on the triplet state of $Z_2$ centres in KCl doped with divalent impurities (Ca$^{++}$, Sr$^{++}$, Ba$^{++}$, Yb$^{++}$) revealed their rather complicated atomistic structure: most probably, an impurity cation — cation vacancy complex is combined with two F centres in various relative positions [1-4]. The simplest atomistic configuration is found with $Z_2^+(Ca)$ and the most frequent type of $Z_2^+(Yb)$ centres: they show pure (100) axial symmetry and are orientable by polarized optical irradiation. The proposed configurational model is simply a divalent cation in (100) nearest neighbourhood to an anion vacancy sharing two electrons with antiparallel spins in the ground state. Few is known on their electronic structure, on the distribution of the electrons onto the constituents of the centre.

$Z_2$ centres can be ionized forming $Z_2^+$ (formerly $Z_3$) centres, that should be paramagnetic. They can then be investigated by means of magnetooptics. $Z_2^+(Ca)$ and $Z_2^+(Yb)$ centres are chosen for the present investigation. Both are orientable in the crystal like the neutral $Z_2$ centres, showing like these a double-band structure in their absorption spectrum. The bands are numbered in order of increasing energy and occur at:

- Ca: $Z_2^+(1): 18.75 \times 10^3 \text{ cm}^{-1}$
- $Z_2^+(2): 20.3 \times 10^3 \text{ cm}^{-1}$
- Yb: $Z_2^+(1): 18.75 \times 10^3 \text{ cm}^{-1}$
- $Z_2^+(2): 20.65 \times 10^3 \text{ cm}^{-1}$

In both cases the $Z_2^+(1)$ band is polarized parallel to the centre axis and possesses by a factor of ~ 2 higher an oscillator strength than the perpendicular transition $Z_2^+(2)$. The magnetooptical experiments are performed with a 5 tesla superconducting magnet at temperatures between 4.2 and 16.0 K. Preparation and handling of the crystals and details of centre formation are described elsewhere [1-3].

2. Results and discussion. — 2.1 The $Z_2^+(Ca)$ centre. — Figure 1a curve 1 shows the absorption spectrum of a KCl : Ca crystal immediately after $Z_2 - Z_2^+$ centre conversion at ~ 100 °C by unpolarized irradiation into the F band region. The low energy peak at $16.8 \times 10^3 \text{ cm}^{-1}$ belongs to $Z_2$ centres, that cannot be avoided in the primary F – $Z_2$ conversion process; a remaining $Z_2$ band peaking at $16 \times 10^3 \text{ cm}^{-1}$ is hidden under the long-wave-

![Fig. 1. — Absorption (a) and MCD (b) spectra of $Z_2^+(Ca)$ centres in KCl before (curves 1) and after (curves 2) their reorientation by the light of the 488 nm line of a mercury high pressure lamp. The MCD is defined by the difference of the absorption indices $K_r - K_l$: $e = (K_r - K_l) d / 2 h c$, $E$: photon energy, $d$: crystal thickness, $h$: Plank's constant/2 $\pi$, $c$: velocity of light.](http://dx.doi.org/10.1051/jphyscol:1980631)
length tail. The two other maxima are the $Z_2^+(1)$ and the $Z_2^+(2)$ bands. Few F centres may still be present too.

Figure 1b curve 1 represents the corresponding magnetic circular dichroism (MCD). It can be decomposed into contributions from $Z_2$, $Z_1$, and F centres in order of increasing energy. Subtracting these out leaves us with the MCD of the $Z_2^+$ centres. It has roughly the shape of a first derivative of the absorption band (but with larger negative tail). Anyway, this behaviour shows anew, that the $Z_2^+(2)$ band represents the perpendicular transitions at the centre, thus confirming earlier statements [1-3]. Apparently, the optical $Z_2^+$ centre formation by irradiation at $18.6 \times 10^3$ cm$^{-1}$ produces mainly centres lying parallel to the direction of the detecting light, and therewith parallel to the magnetic field. Assuming in a first attempt an s-p,$p_z$ transition being responsible for the perpendicular $Z_2^+$ band allows an evaluation of the spin orbit energy $A_{xy}$ and of an orbital $g$ factor by a rigid shift analysis using the temperature dependence of the high energy minimum only:

$$A_{xy} = -8.8 \text{ meV}, \quad g_{orb}^{xy} = 0.65.$$

Essential input data are the maximum optical density $D_{\text{max}} = 0.65$ and the half width $W_{1/2} = 0.174$ eV of the $Z_2^+(2)$ band.

Shining unpolarized light into the $Z_2^+(2)$ band at $-100 \, ^\circ\text{C}$ reorients the centres until they finally all lie perpendicular to the direction of the light beam: Figure 1a, curve 2. The $Z_2^+(2)$ band decreases and the $Z_2^+(1)$ band increases. The change in the corresponding MCD spectrum (Fig. 1b, curve 2) is more drastic. As essential effect we emphasize, that the high energy minimum has now the shape of an absorption band. The magnetic perturbations induce an exchange in area between the $Z_2^+(2)$ and the $Z_2^+(1)$ band. Under analogous assumptions as above and using the area exchange formula of reference [5] we deduce again from the temperature dependence of this exchange:

$$A_{xx} = -8.9 \text{ meV}, \quad g_{orb}^{xx} = 0.4.$$

The input data are now an optical density $D_{\text{max}}(Z_2^+(2)) = 0.35$, the ratio of the oscillator strengths $f_1/f_2 = 1.8$ as determined earlier [1] and the energy distance

$$E_2 - E_1 = 1550 \text{ cm}^{-1} = 0.192 \text{ eV}.$$

The coincidence of both results is surprising and certainly fortuitous. We admit at least an uncertainty of 20%. The most essential result is the negativity of the spin orbit splitting, its size being similar to that of the F centre with $-10 \text{ meV}$. The $Z_2^+$ centre is a perturbed F centre looking most probably like the $F_A$ centre, the «A-atom» in this case being the Ca$^{++}$ impurity.

Nevertheless some points need to be mentioned:

a) There is no conservation in absorption area ($\Delta A = A_r - A_i < 0$), as expected for magnetic perturbations [5]. Apparently not all $Z_2^+$ centre absorptions are recorded.

b) The high energy MCD minimum in the perpendicular case occurs at $20.7 \times 10^3$ cm$^{-1}$ and does not coincide with the $Z_2^+(2)$ band maximum. This may be due to some remaining parallel centres or to a non-resolved magnetic substructure in the MCD bands, very much smaller but similar to that found below for the $Z_2^+(Yb)$ centre.

c) The energetic positions (shift to higher energies) of both $Z_2^+$ bands relative to the F and $F_A$ bands remain unexplained.

2.2 THE $Z_2^+(Yb)$ CENTER. — The same optical conversion as above yields the absorption spectrum of figure 2a, curve 1 for the $Z_2^+(Yb)$ centres. Besides the $Z_1$ and a rest $Z_2$ band a not very marked $Z_2^+$ centre spectrum is visible. The centres are expected to occur again in the parallel orientation only.

![Figure 2](image-url)

Fig. 2. — Absorption and MCD of $Z_2^+(Yb)$ centres in KCl before (curves 1) and after (curves 2) their reorientation. Besides the $Z_1$ centres MCD a very small F centre MCD hides two even smaller $Z_2^+$ centre transitions.

The corresponding MCD spectrum figure 2b, curve 1 is surprising. In spite of the smooth and weak absorption there is a large and well-structured MCD, beginning with a positive wiggle at high energies. Eliminating the $Z_1$ centre MCD at the low energy end of the spectrum, one finds 4 extrema belonging to $Z_2^+(Yb)$. Orienting the centres perpendicular to the light beam produces the spectra of figure 2a and b, curves 2.
Now the MCD pattern contains 5 extrema. Again the zeroth moment change is negative in both cases.

This structure can never be explained by a simple \(\text{s-p transition perturbed by a crystal field of } C_{4v} \) symmetry. The 5-peak structure points towards a \(\text{d-state, and such a d-state is available as the lowest excited state of the Yb}^+ \) ion. At first sight one is led to the idea of interpreting the ensemble of \( Z_2^+ (\text{Yb}) \) bands as due to an \( s-d \) transition, the electron charge being transferred from an \( s\)-like \( F \) centre ground state to a \( d\)-like impurity excited state. The splitting of the bands is then explainable by a crystal field of \( C_{4v} \) symmetry and a spin orbit interaction \( \text{ILS} \).

A simple model calculation shows, that the structure of the MCD pattern figure 2b can only be understood by taking into account a small negative contribution to the spin orbit effect due to the \( F \) centre and a large positive contribution due to the \( \text{Yb}^+ \) ion: the result is a spin orbit splitting of \(+ (100 - 125) \text{ meV}\) for the \( Z_2^+ (\text{Yb}) \) centre.

**DISCUSSION**

**Question. — A. Winnacker.**

I don't see how you can have a spin orbit splitting between \( x \)- and \( y \)-states in a centre of \( Z \) symmetry. The matrix elements \( \langle x | \Delta \text{SL} | x \rangle \) and \( \langle y | \Delta \text{SL} | y \rangle \) are just the same.

**Reply. — H. J. Paus.**

This is right; but the selection of the circularly polarized transitions is only possible via the magnetic field; then — roughly speaking — the energy difference of the position of the right and left circularly polarized absorption band gives the spin orbit splitting.

**Question. — V. V. Ratnam.**

1) The model of \( Z_2 \) centre taken by you (Dr. Paus) is that of Okhura, whereas the one used by Dr. Strohm is the same but with an IV-complex adjacent to it. Taking the results with both impurities together we are inclined to believe, that the truth lies halfway between both models: the excited \( Z_2^+ \) centre state is a \( p/d \) hybride explaining immediately the intense parallel transition (\( \sigma_{\text{overlap}} \)) as compared to the less strong perpendicular ones (\( \pi_{\text{overlap}} \)). As easily seen the hybridization is also responsible for the shift to higher energies of all \( Z_2^+ \) centre transitions relative to those of the \( F \) centre. The formerly proposed atomistic model is confirmed.

Similar arguments should hold for the neutral \( Z_2 \) centre by taking its two-electron character into account. Here also the excited state should be represented by a hybridized \( p/d \) wave function explaining similarly as above the ratio of the oscillator strengths \( j_{\pi}/j_{\sigma} \).

Looking over the whole family of \( Z \) centres in \( \text{KCl} \) we remember the case of the \( Z_2 (\text{Ba}) \) centre with its outstanding two-band structure, now understandable in the same framework from the extremely low-lying \( d \)-state of the \( \text{Ba}^+ \) ion.

**References**