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How to cite

BILL, Hans, LOVY, Dominique, HAGEMANN, Hans-Rudolf. Study of the T⊗t Jahn-Teller effect: ESR of Ag2+ in the alkaline earth fluorides. In: Solid state communications, 1989, vol. 70, n° 5, p. 511–516. doi: 10.1016/0038-1098(89)90941-1

This publication URL:https://archive-ouverte.unige.ch/unige:3072Publication DOI:10.1016/0038-1098(89)90941-1

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STUDY OF THE T&T JAHN-TELLER EFFECT : ESR OF Ag²⁺ IN THE ALKALINE EARTH FLUORIDES

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(Received January 31, 1989 by R. H. Silsbee)

ESR results are reported on the Ag^{2+} ion introduced into alkaline earth fluoride crystals. In SrF_2 (as in CaF_2) a trigonal centre is present which tunnels between four equivalent C_3 directions as shown by ESR under uniaxial stress. A $T_{2g} \otimes t_{2g}$ Jahn-Teller model describes adequately the paramagnetic and stress effects when the strong coupling case is considered. Ag^{2+} in BaF_2 forms a static tetragonal cluster similar to Ag^{2+} and Cu^{2+} in $SrCl_2$.

Comparatively few experimental ESR studies have been published on Jahn-Teller (JT)-systems which involve a $T_{2g} \otimes t_{2g}$ situation. Looking for possible candidates we revisited the long-standing problem to introduce silver and copper into the alkaline earth fluorides. It turns out that they enter into the lattice when oxygen is absent during crystal growth. This letter reports ESR results including uniaxial stress measurements on these crystals.

Crystals were obtained under very high purity conditions in a Bridgman furnace. Nominal doping concentrations were 0.3 to 1 mole % of AgF. Much of the silver fluoride decomposes during growth. Further, the distribution of the Ag ions in the as-grown crystals was not homogeneous. Samples were cleaved off or cut with a string saw. They are colourless and transparent and their absorption spectrum presents two bands in the UV. At and above 4.2K no ESR signal related to silver was observed. After exposing them to Xrays, for typically 1 h (40 kV/35 mA, room temperature), all of the samples became yellow-brownish. The optical absorption spectrum shows strong new absorption bands in the visible and near UV . At the same time a strong ESR spectrum is observed. We assign it to Ag^{2+} as will be shown below. The spectra observed in SrF_2 and CaF_2 are very different from those in BaF2 and we will treat each case in turn.

$\frac{\mathrm{SrF}_2 : \mathrm{Ag}^{2+}}{\mathrm{These}}$

These crystals exhibit at 4.2K a strong and anisotropic spectrum. Its

angular dependence was investigated as a function of the orientation of the magnetic field. The spectra observed with B along C_4 , C_3 and C_2 , respectively, are shown in Fig. 1. Their structure and the intensity distribution of the components are well explained by assuming a spin S = 1/2, with an associated g-tensor oriented along a body diagonal of the host unit cell, which interacts strongly with two always equivalent F ions and less with six fluorine nuclei. These latter ones produce mutually equivalent splitting when the magnetic field is parallel to the principal axis of g. In addition, S interacts with one nuclear spin I = 1/2(the silver nucleus; two isotopes exist but were not resolved : 10^{7} Ag : 51.82%, 10^{9} Ag : 48.18%, both I = 1/2). The observed lines are symmetrical, of Gaussian shape with a typical width $B_{pp} \simeq 2.6$ Gauss. The relaxation times of the centre are comparatively short as the ESR spectrum broadens and disappears between 9 and 18 K. Above 18K no signal related to silver could be found.

The centre has D_{3d} symmetry. It consists of an Ag^{2+} ion substituting for a host cation in a cube formed by eight F⁻ ions. This structure is trigonally deformed in the sense that two opposing fluorine ions on a body diagonal approach the silver ion whereas the six others seem to recede. The two former ones have each local symmetry C_{3V} (axial shf tensor) and the latter ones have C_{5} local symmetry. A trigonal spin Hamiltonian was

A trigonal spin Hamiltonian was used to parametrize the ESR spectra. A preliminary first order analysis yielded the approximate starting



Fig. 1. ESR spectra of Ag^{2+} in SrF₂ observed with B as noted. T = 4.2 K. Microwave frequency : 9.101 GHz (C_2, C_4) , 9.195 GHz (C_3) .

parameters for our computer programs which allow a complete second order analysis with graphical representation of the results. The parameters thus obtained are given in the Table. Yet, the experimental results are also compatible with an Ag^{2+} ion substituting for a fluorine ion and being associated with two F ions, one interstitial and the other one being located on a Sr cation site. It can also be viewed as a AgF₂ molecule

inbedded into the crystal. CaF_2 : Ag^{2+} presents the same symmetry properties as SrF_2 : Ag^{2+} . In the course of this work we became aware of ref [1] where ESR of Ag^{2+} in CaF_2 and CdF_2 is reported. These data are consistent with our results consistent with our results.

In order to decide between the possible interpretations we performed ESR under uniaxial stress applied to the sample. Both centres, $CaF_2:Ag^{2+}$ and $SrF_2:Ag^{2+}$, do not show any effect when stress is applied along a [001] crystal axis. Important modifications are seen, however, when stress along [111] is used. Strong and fully reversible repopulation is found such that the trigonal axis of the centre is preferentially oriented parallel to the applied stress. Figure 2 shows results for both hosts obtained under the geometry explained in the figure caption.

In view of these facts the geometrical structure shown in Fig. 3a is proposed for SrF_2 : Ag^{2+} and CaF_2 : Ag^{2+} .

<u>BaF₂ : Ag²⁺.</u> A spectrum is observed (among weaker ones) which involves a spin S = 1/2 interacting with several F neighbours and one silver nucleus. But the symmetry of the g-tensor is <u>tetragonal</u>. Fig. 4 presents ESR spectra recorded with B parallel to a C_4 , C_3 , C_2 axis, respectively. The detailed añalysis of the angular dependence discloses a C_{4v} symmetry of the paramagnetic cluster. Resolved hyperfine interaction with the Ag nucleus (tetragonal symmetry) and with two sets of F neighbours, each containing four equivalent ions, is observed. Each of these latter nuclei has C_s symmetry. The parametrization procedure which is similar to the one described above (but using the appropriate spin Hamiltonian) yielded the constants given in the Table, whereas Fig. 3b shows the structure of the centre we propose and defines the orientations of the tensors.

This paramagnetic centre exhibits much longer relaxation times than SrF_2 : Ag^{2+} as its ESR signals are observed at and above 78K. At 4.2K they saturate heavyly even at 10^{-5} Watt nominal microwave power. No effects due to applied stress were observed on this

system. An ENDOR study is planned. The structure of this centre is similar to the Ag^{2+} and the Cu^{2+} in SrCl₂ [2,3] which equally did not show any stress effects.

STUDY OF THE TS JAHN-TELLER EFFECT

Table : ESR parameters of the Ag^{2+} centers.

host
SrF₂
$$g_{\parallel} = 1.9201 (5)$$
 Ag nucleus
 $g_{\perp} = 2.5825 (8)$ $A_{\parallel} = 20.7 (3)$
 $A_{\perp} = 23,2 (3)$
F₁, F₂ $A_{\parallel} = 697.3 (259.2 G)$
 $A_{\perp} = 24.78 (6.85G)$
F₃ - F₈ $A_{11} = 41.3$
 $A_{22} = 28.9$ $d = 28^{\circ}$
 $A_{33} = 86.2$

BaF₂:
$$g_{\parallel} = 2.4592$$
 (8) Ag nucleus
 $g_{\perp} = 2.0836$ (10) $A_{\parallel} = 98(3)$
 $A_{\perp} = 78(3)$

superhyperfine structure

Set	1		Set 2
A ₁₁	= 77	(8)	$A_{11} = 20(3)$
A ₂₂	= 102	(8)	$A_{22} = 20(3)$
A ₃₃	= 648	(5)	$A_{33} = 5(2)$
ያ	'= 7 ⁰ (1		6 [#] = 52 ⁰ (3)

hf and shf const. in [MHz]

<u>Discussion</u>.

A. SrF_2 : Ag^{2+} . The ground state of Ag^{2+} in cubic coordination transforms as T_{2g} and is thus JTactif. Within the weak covalency approximation the orbital part consists essentially of $(4d_{YZ}, 4d_{ZX}, 4d_{XY})$ The experiments indicate that the electronic triplet couples with trigonal vibrations. Within a (AgF_8) cluster model there are two local vibrations transforming as t_{2g} . Again the experimental results tend to show that the dominantly radial one (Fig. 1 f of [3]) is important. Thus, we can apply the (cubic) $T_{2g} \otimes t_{2g}$ model [4] to this centre. The four adiabatic JTpotential minima in the threedimensional vibrational space are deep enough (and equivalent within our experimental findings) to produce a pseudostatic JT effect as indicated by the fact that the centre reorients, but has conventional lineshapes and trigonal symmetry. It is therefore appropriate to transform from the vibronic ($T_{1g} + A_g$) quadruplet state to eigenstates located in each of the wells. Then, the theory of the g tensor developped in [5] is appropriate after T = 4.2 K



Fig. 2. Effect of uniaxial stress applied along a [111] axis of

- (a) CaF_2 : Ag^{2+}
- (b) SrF_2 : Ag^{2+}

and observed on the ESR spectrum with B || $[\overline{112}]$. n_{\parallel} = intensity of the spectral components associated with p||C₃ and $n_{70.7}$ = same quantity but with p along one of the three other C₃ axes. The ratio (slope (b))/(slope (a)) = 1.47(9). The experimental energy per unit stress (AE_1) for this geometry is

CaF₂ \mathbf{A} E₁ = 2.62 \cdot 10⁻⁶ [cm⁻¹/Pa] 5.204 \cdot 10⁻²⁹ [J/Pa] SrF₂ \mathbf{A} E₁ = 3.85 \cdot 10⁻⁶ [cm⁻¹/Pa] 7.65 \cdot 10⁻²⁹ [J/Pa]

With :
$$\Delta E_1 = \frac{KT}{P} \ln (n_{11}/n_{70.7})_P$$

a few minor modifications (under progress). The strongly negative value g_{||} - 2.0023 = -0.0822 indicates that covalency is not negligible. The fact that no motionally

averaged spectrum was found is probably due to the (strongly quenched) spinorbit coupling being important in the reorientation process between the different potential sheets [6]. As a result the spatial reorientation produces important contributions to the spin relaxation [7].



- Fig. 3. a) Geometrical model of Ag^{2+} in SrF_2 . The Ag^{2+} ion is at the center of the cube. $F_{1,2}$ are the axial fluorine ions. The shf tensor axes of F_3 are shown. The others are obtained by applying transformations $\{R\} \notin D_{3d}$.
 - b) Structure of Ag^{2+} in BaF_2 . The Ag^{2+} approaches the base plane. The shf tensor axes of one fluorine ion of each set are shown. The axes labeled 1 and 3, respectively, are located in the vertical diagonal plane.



Fig. 4. ESR spectra of Ag^{2+} in BaF_2 . B oriented as noted. Microwave frequency : 9.258 GHz.

B. The silver center in BaF₂ :its structure is remarkably different from the ones observed in SrF₂ and CaF₂. It forms an almost flat quadratic pyramid with the silver ion being located at the apex. Choosing axes parallel to the fourfold crystal axes one has essentially a $4d_{xy}$ orbital of the magnetic electron. The well-known relation that $g_{||} - 2.0023 > g_{\perp} - 2.0023$ complies with the experimental results. It is possible that the different behaviour is due to the larger unit cell, and the smaller ionic radius of

Ag²⁺ as compared to Ba²⁺, resulting in a much smaller trigonal JT coupling constant (the tetragonal one is anyhow small), which leads to an "adsorption" of the silver ion on a surface of the surrounding fluorine cube. Note that this coordination is typical for many d⁹ coordination complexes.

The authors acknowledge a discussion with Prof. Ch. Joergensen. This work was supported by the Swiss National Science Foundation.

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