

SILVER IMPURITIES IN CUBIC METAL FLUORIDES. JAHN–TELLER EFFECTS IN $4d^9 5s^1$ AND $4d^9$ MULTIPLETS

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Abstract. Silver was introduced into several metal fluorides with the aim to generate different Jahn–Teller (JT) situations. Optical absorption and luminescence experiments involving the ground $4d^{10}$ and the excited $4d^9 5s^1$ configuration of Ag^+ revealed a weak $T \otimes e$ JT effect in the (approximately) T_2 excited triplets in NaF and SrF_2 , but much stronger differences between different hosts in the (approx.) E doublet. The strongest effect was observed in the host NaF. The theoretical developments initiated by Wagner have given the best interpretation of the observed temperature dependence of optical line shapes. EPR experiments (in part with a sample under uniaxial stress) on Ag^{2+} in MeF_2 crystals (Me: Ca, Sr, Ba) and SrCl_2 demonstrated the action of a $T_2 \otimes t_2$ JT effect for the former two hosts and, probably, a quadratic JT effect or an off-centre situation for the latter two. The experimental results and models are presented.

Key words: impurity centres, triplet Jahn–Teller effect, Jahn–Teller-induced relaxation, Jahn–Teller effect in excited states, fluoride hosts (cubic).

INTRODUCTION

Monovalent silver and copper ions have been entered successfully into most of the alkali halides and these systems have extensively been studied, e.g. [1, 2]. Alkali fluoride hosts are noteworthy exceptions. It is difficult to produce usefully doped crystals, because at higher temperatures silver fluorides are unstable. To an even higher degree similar problems are met with during the preparation of silver-doped alkaline earth fluorides. A strongly inhomogeneous distribution of silver has usually been observed [3, 4]. The nd^{10} ions are model systems for the study of nontrivial excited state structures of impurity ions in ionic crystals and the results obtained may serve as test data against numerical results of quantum-mechanical modellings. Cu^+ in NaF is among the most studied systems and a wealth of information through very detailed optical investigations [5] is available. But it is still not fully understood. The investigation of Ag^+ was initiated

because of expected similarities but also differences, in particular regarding a possible competition between the JT effect and spin-orbit coupling. The motivation for introducing this ion into alkaline earth fluorides was initially based on the expectation to produce the Ag^{2+} ion in cubic surroundings. Its existence has been established for CaF_2 , SrF_2 [6, 7], in particular as regards the involvement of a $T_{2g} \otimes t_{2g}$ -type JT effect [7]. However, it is only observed in crystals previously X-rayed. In addition, the irradiated samples always contained a variety of other silver-related microscopic centres which produce numerous optical absorption bands between 800 and 200 nm, not directly related to the JT Ag^{2+} ion [3].

The paper presents the results related to different JT situations of Ag^+ and Ag^{2+} in alkaline earth fluorides. Details of the crystal growth and of our experimental procedures are given, e.g. in [3].

RESULTS AND DISCUSSION

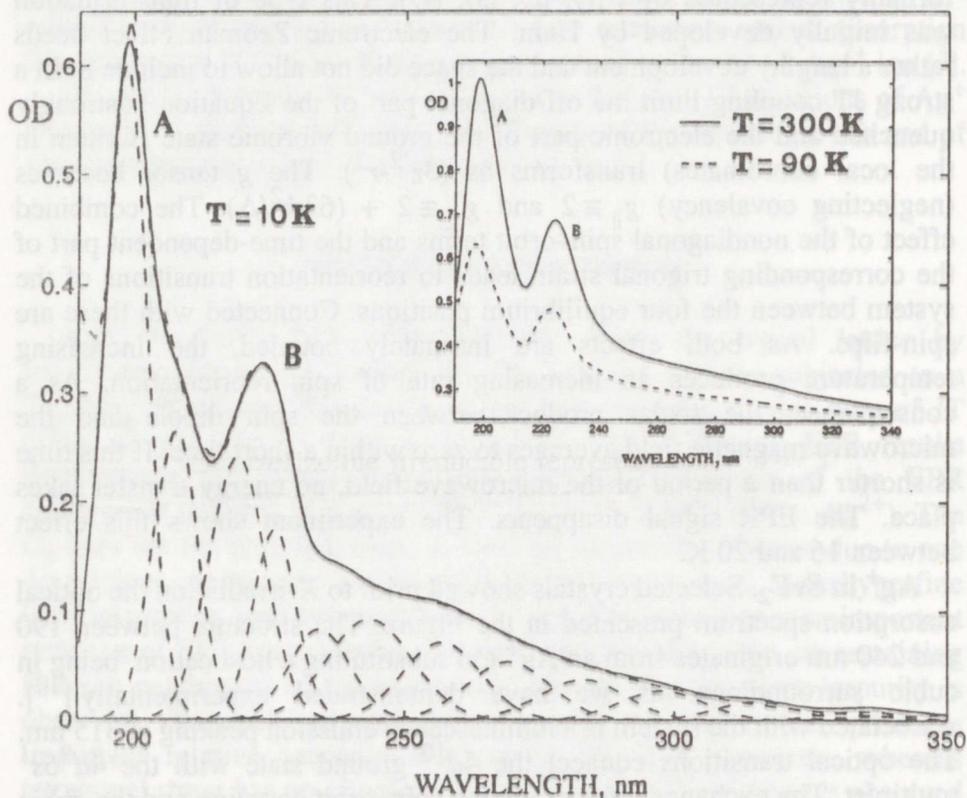
Ag^{2+} in CaF_2 , SrF_2 . The impurity enters the crystal lattice by substituting for a host cation. Its $^2T_{2g}$ ground state is subjected to a $T_{2g} \otimes t_{2g}$ JT effect. This is one of the rare examples of this type of JT effect in the ground state with $S = 1/2$. The following EPR results demonstrate this model [6, 7]. The angular dependence of the EPR spectrum is trigonal with $g_{\parallel} = 1.9201$ and $g_{\perp} = 2.5825$ (SrF_2 : Ag^{2+}). The C_3 axes are the principal ones. A resolved hyperfine structure due to one Ag nucleus can be seen. The isotope effect is not resolved. Superhyperfine (shf) interaction with two equivalent F^- neighbours produces an important structure of EPR lines. Much smaller shf structure due to the six remaining fluorine neighbours of the anion cube surrounding the silver impurity is observed. Trigonal uniaxial stress applied to the crystal produces important relative intensity changes in the EPR spectrum, whereas tetragonal stress has no effect at all. Finally, the EPR spectrum is observed only below 16–20 K. Above this temperature no signal was seen, in particular no motionally averaged one. A cluster JT model [8, 9] involving strong coupling to a trigonal effective mode may be used. It implies an almost degenerate vibronic ground quadruplet ($A_{1g} + T_{2g}$) by approximately $0.8 h\nu$ below the mutually very close $T_{1g} + T_{2g} + E_g$ vibronic levels. The adiabatic potential of the model has four minima which correspond to the four trigonal deformations of the cube. Thereby the two F^- ions on the corresponding axis approach the silver ion and a kind of linear $(\text{F}-\text{Ag}-\text{F})^\circ$ molecule is formed. The EPR results may be discussed with the aid of an effective Hamiltonian (H_{eff}) within the vibronic ground quadruplet multiplied by $D_{1/2}$. We write $|\xi v\rangle$, $|\eta v\rangle$, $|\zeta v\rangle$ for the vibronic orbital states of the T_{2g} level and $|a_1 v\rangle$ for the one transforming as the A_{1g} vibronic state, and include the following terms into H_{eff} :

$$H_{\text{eff}} = 4\Gamma |a_1 v\rangle \langle a_1 v| + \lambda \mathbf{L} \cdot \mathbf{S} + V_i (u_\xi \varepsilon_\xi + u_\eta \varepsilon_\eta + u_\zeta \varepsilon_\zeta) + \beta_0 \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B}.$$

In this order the terms are: the tunnel splitting (diagonal in the spin), the spin-orbit interaction, the trigonal strain (where the u are the T_{2g} matrices within the electronic triplet level), and the electronic Zeeman effect. Note that the u evaluated within the vibronic states produce reduction factors. The matrix built up from the first three interactions is given in the Appendix. It was obtained by transformation from the symmetry-determined basis ($|\xi v\rangle, |\eta v\rangle, |\zeta v\rangle, |a_1 v\rangle$) to a localized vibronic basis, formally represented by ($|1\rangle, |2\rangle, |3\rangle, |4\rangle$). This type of transformation was initially developed by Ham. The electronic Zeeman effect needs rather a lengthy development and the space did not allow to include it. In a strong JT coupling limit the off-diagonal part of the Equation is strongly quenched and the electronic part of the ground vibronic state (written in the local coordinates) transforms as $(3z'^2-r^2)$. The g tensor becomes (neglecting covalency) $g_{\parallel} \cong 2$ and $g_{\perp} \cong 2 + (6\lambda k^2/\Delta)$. The combined effect of the nondiagonal spin-orbit terms and the time-dependent part of the corresponding trigonal strain leads to reorientation transitions of the system between the four equilibrium positions. Connected with these are spin-flips. As both effects are intimately coupled, the increasing temperature produces an increasing rate of spin reorientation. As a consequence, the scalar product between the spin dipole and the microwave magnetic field averages to zero within a short time. If this time is shorter than a period of the microwave field, no energy transfer takes place. The EPR signal disappears. The experiment shows this effect between 16 and 20 K.

Ag⁺ in SrF₂. Selected crystals showed prior to X-irradiation the optical absorption spectrum presented in the Figure. The structure between 190 and 240 nm originates from an Ag⁺ ion substituting a host cation, being in cubic surroundings, as we have demonstrated experimentally [10]. Associated with the system is a luminescence emission peaking at 315 nm. The optical transitions connect the $4d^{10}$ ground state with the $4d^9 5s^1$ multiplet. The exchange interaction, the spin-orbit coupling and the cubic crystal field split this level into ($A_{2g} + E_g + 2T_{1g} + 2T_{2g}$ (from ${}^3D_1 + {}^3D_2 + {}^3D_3$) and $E_g + T_{2g}$ (from 1D_2)). We wrote down the 20×20 matrix of these interactions and obtained the following parameters by fitting the solutions to the spectra of Figure: $\lambda = 1203 \text{ cm}^{-1}$, $K = 1597 \text{ cm}^{-1}$, $10Dq = 3195 \text{ cm}^{-1}$. Due to the small crystal field value there is sizable mixing of the spin singlet and triplet character of the levels. Particularly strong singlets are the E_g (94.5% singlet character) at 50400 cm^{-1} and two T_{2g} levels (each approx. 50%) at 48200 cm^{-1} and 45600 cm^{-1} , respectively. All the three levels are candidates for the JT effect. We admit that each of them can be treated independently. The doublet implies the optical transitions $A_1 \leftrightarrow E \oplus (e + a_1)$, considered theoretically by Wagner [11], Vekhter et al. [12] and others [13]. Their model predicts a line shape depending on the ratio of the coupling constants to the e and the a_1 mode frequency, respectively. For large values of the ratio an asymmetric doublet is predicted and an almost symmetrical single line is obtained in the other limit. Our analysis of the experimental spectrum shows that this ratio is smaller than 0.1 with an effective frequency of the symmetrical

mode of $\nu \cong 185 \text{ cm}^{-1}$. This result is reasonable because the local effective e mode implies a tangential movement of the ligands around the silver ion with a concomitantly small JT coupling constant. A different situation was observed for Ag^+ in NaF. There this latter coupling constant is large and a resolved asymmetric doublet structure of the corresponding optical transition was observed. Detailed results will be published [14].



Absorption spectrum, $T=10 \text{ K}$. $\text{SrF}_2:\text{Ag}^+$, plate of 2.2 mm thickness. Spectral decomposition into elementary gaussian bands (---- experimental, — fitted spectrum). Insert: absorption spectrum of a $\text{SrF}_2:\text{Ag}^+$ plate (3.2 mm) at $T=300, 90 \text{ K}$.

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Appendix

The Equation gives the spin-orbit coupling, trigonal strain and the tunnel splitting within the localized vibronic functions obtained by a base change from the $A_{1g} + T_{2g}$ subspace. $f(T_1)$ is a reduction factor, V and V' are the reduced matrix element multiplied by reduction factors, the basic ε are the T_{2g} strain parameters. They contain a static and a randomly time dependent part.

$ 1+\rangle$	$ 1-\rangle$	$ 2+\rangle$	$ 2-\rangle$	$ 3+\rangle$	$ 3-\rangle$	$ 4+\rangle$	$ 4-\rangle$
$\Gamma + v\varepsilon_4$		$\Gamma + w\varepsilon_\zeta$	$-u(1+i)$	$\Gamma + w\varepsilon_\zeta + iu$	u	$\Gamma - w\varepsilon_\eta - iu$	iu
	$\Gamma + v\varepsilon_4$	$u(1-i)$	$\Gamma + w\varepsilon_\zeta$	$-u$	$\Gamma + w\varepsilon_\zeta - iu$	iu	$\Gamma - w\varepsilon_\eta + iu$
		$\Gamma + v\varepsilon_3$		$\Gamma + w\varepsilon_\eta - iu$	$-iu$	$\Gamma - w\varepsilon_\zeta + iu$	$-u$
			$\Gamma + v\varepsilon_3$	$-iu$	$\Gamma + w\varepsilon_\eta + iu$	u	$\Gamma - w\varepsilon_\zeta - iu$
				$\Gamma + v\varepsilon_2$		$\Gamma - w\varepsilon_\zeta$	$u(1-i)$
					$\Gamma + v\varepsilon_2$	$-u(1+i)$	$\Gamma - w\varepsilon_\zeta$
						$\Gamma + v\varepsilon_1$	
							$\Gamma + v\varepsilon_1$

$$v = \left(\frac{V}{2} + \frac{V'}{2} \right), \quad w = \left(\frac{V}{2} - \frac{V'}{2} \right), \quad \varepsilon_1 = (\varepsilon_\xi + \varepsilon_\eta + \varepsilon_\zeta), \quad \varepsilon_2 = (-\varepsilon_\xi - \varepsilon_\eta + \varepsilon_\zeta), \quad \varepsilon_3 = (\varepsilon_\xi - \varepsilon_\eta - \varepsilon_\zeta),$$

$$\varepsilon_4 = (-\varepsilon_\xi + \varepsilon_\eta - \varepsilon_\zeta), \quad u = f(T_1) \frac{\lambda}{4}$$

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HÖBEDA LISANDID KUUBILISTES METALLFLUORIIDIDES. JAHNI-TELLERI EFEKT $4d^9 5s^1$ - JA $4d^9$ -MULTIPLETTIDES

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Metallfluoriidide koostisse on sisse viidud hõbe eesmärgiga tekitada erinevaid Jahni–Telleri efekti (JTE) situatsioone. Optilise neeldumise ja luminesentsi eksperimendid, kus osalevad põhikonfiguratsioon $4d^{10}$ ja ergastatud konfiguratsioon $4d^9 5s^1$, näitavad nõrka ($T \otimes e$)-JTE ergastatud T_2 -tripletis NaF ja SrF_2 kristallides, kuid E -dubleti erinevused erinevates kristallides on palju tugevamad. Kõige tugevam on see efekt NaF kristallis. Optilise spektrijoone kuju temperatuurisõltuvuse parima tõlgenduse on andnud Wagneri algatatud teoreetilised käsitlused. EPR-eksperimendid (osaliselt kristalliga ühesuunalise rõhu all) Ag^{2+} -ga MeF_2 (Me: Ca, Sr, Ba) ja $SrCl_2$ kristallides demonstreerisid ($T_2 \otimes t_2$)-JTE esimeses kahes kristallis ja tõenäoselt kvadraatset JTE või mittesentraalset situatsiooni kahes viimases. On esitatud eksperimentaal-andmed ja mudelid.

ПРИМЕСИ СЕРЕБРА В КУБИЧЕСКИХ ФТОРИДАХ МЕТАЛЛОВ. ЭФФЕКТ ЯНА–ТЕЛЛЕРА В $4d^9 5s^1$ - И $4d^9$ -МУЛЬТИПЛЕТАХ

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Серебро введено в несколько фторидов металлов для создания разных ситуаций эффекта Яна–Теллера (ЭЯТ). Эксперименты по оптическому поглощению и люминесценции, связанные с основной $4d^{10}$ и возбужденной $4d^9 5s^1$ конфигурациями, проявили слабый ($T \otimes e$)-ЭЯТ в возбужденном T_2 -триплете в кристаллах NaF и SrF_2 , и более сильные различия для разных кристаллов в E -дублете. Наиболее сильный эффект наблюдался в кристалле NaF. Наилучшая интерпретация наблюдаемых температурных зависимостей контуров оптических линий дана теоретическими работами, начатыми Вагнером. ЭПР-эксперименты (частично с кристаллами под одноосным сжатием) по Ag^{2+} в кристаллах MeF_2 (Me:Ca, Sr, Ba) и $SrCl_2$ выявили ($T_2 \otimes t_2$)-ЭЯТ в первых двух кристаллах и, вероятно, квадратичный ЭЯТ, или внецентровую ситуацию, в последних двух. Представлены экспериментальные результаты и модели.