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Lefèvre, Valérie; Monnier, Alain; Schnieper, Marc; Lovy, Dominique; Bill, Hans

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Defect Association, Jahn-Teller or Off-center Effect in CaF_2: Copper, BaF_2: Silver?*

By V. Lefèvre, A. Monnier†, M. Schnieper, D. Lovy and H. Bill

Université de Genève, Groupe CPB, Sciences II,
30, Quai E. Ansermet, CH-1211 Genève 4, Switzerland

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Transition metal impurity (71.55 He) / Condensed matter spectroscopy (78.50-w) / EPR / ENDOR (76.30) / Strain splitting (71.70 Ej) / Jahn-Teller effect

The results of a detailed optical and paramagnetic-resonance study performed on copper in CaF_2 and silver in BaF_2 are presented. Two different Ag^+ centers were identified in BaF_2. One is associated with an interstitial F^- ion whereas the other one has a cubic surrounding. The Cu^{2+} ion in CaF_2 was shown to reorient at 4.2 K between 6 equivalent minima of D_{2h} symmetry. This fact is interpreted with the aid of a $T_{2g}\otimes(T_{2g}+E_g)$ type Jahn-Teller effect. The nonlinear mixed coupling terms are shown to play an important role. The Cu^+ impurity in CaF_2 is presumably off-center in the F^- sublattice without associated defect or impurity.

I. Introduction

Silver and copper ions introduced into the cubic alkaline-earth halide hosts show diverse and interesting manifestations of the Jahn-Teller effect, essentially because basically a cubic (as opposed to the usual octahedral) surroundings acts, a variety of ratios between the impurity radius and the host lattice constant may be realized and because the CaF_2 lattice is an open structure. The Ag^{+2} ion introduced under suitable crystal growth conditions into the CaF_2 or SrF_2 host represents one of the very few systems where the ground state exhibits an intermediate to strong $T_{2g}\otimes t_{2g}$ Jahn-Teller effect [1, 2]. This was demonstrated with the aid of EPR experiments performed under uniaxial stress [2]. The $4d^{10}\,5s^0 \Leftrightarrow 4d^9\,5s^1$ optical transitions of the Ag^+ ion in these same hosts were investigated by absorption and luminescence spectroscopy [3]. They are well explained when a cubic surroundings of the $^1A_{1g}$ ground state is assumed.

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† Alain Monnier deceased untimely at the age of 34 years on August 19th 1996.

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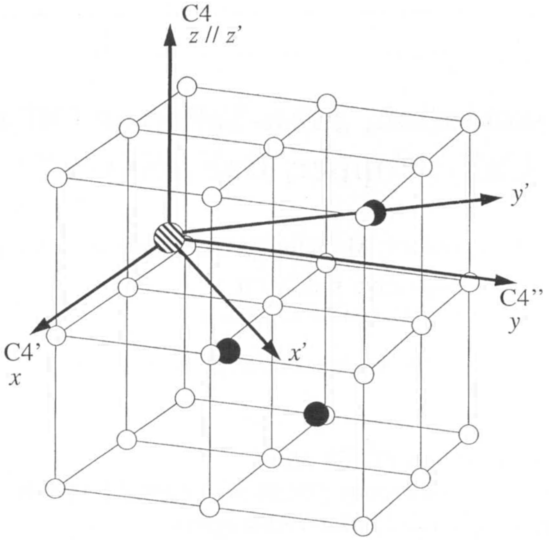

Fig. 1. Schematic structure of the CaF_2 lattice with a cationic impurity. Not shown are the different charge compensation situations (see text). Atoms: black disk: host cation (Ca), open disk: fluorine ion, hatched disk: Cu ion.

The situation is less clear regarding Copper in CaF_2 and Silver in BaF_2. The system $BaF_2{:}Ag^{2+}$ exhibits a tetragonal [2] EPR spectrum due to an associated impurity. No publication seems to exist regarding the Ag^+ ion in this host. We identified its optical absorption and luminescence spectrum and investigated their temperature dependence. Results will be presented in this paper.

Experimental results on Cu^{2+} and Cu^+ in CaF_2 were published by several groups. An EPR investigation by Zaripov *et al.* [4] showed that the former ion ($3d^9$) is substituting for a host cation. The analysis of the super hyperfine structure of the spectrum allowed to establish that Cu^{2+} together with its F^- neighbours forms a complex of D_{2h} symmetry. But the model remained open to questions. A spectroscopic study of the $3d^{10}\,4s^0 \Leftrightarrow 3d^9\,4s^1$ transitions of $CaF_2{:}Cu^+$ [5] demonstrates that the Cu^+ ion is off-center. We will present new experimental results allowing to clarify certain aspects of these models.

II. Experimental

All the crystals investigated were grown in our Laboratory in a Bridgman type furnace and under high purity condition. Residual impurities could always be traced back to the starting materials. Optical absorption spectra

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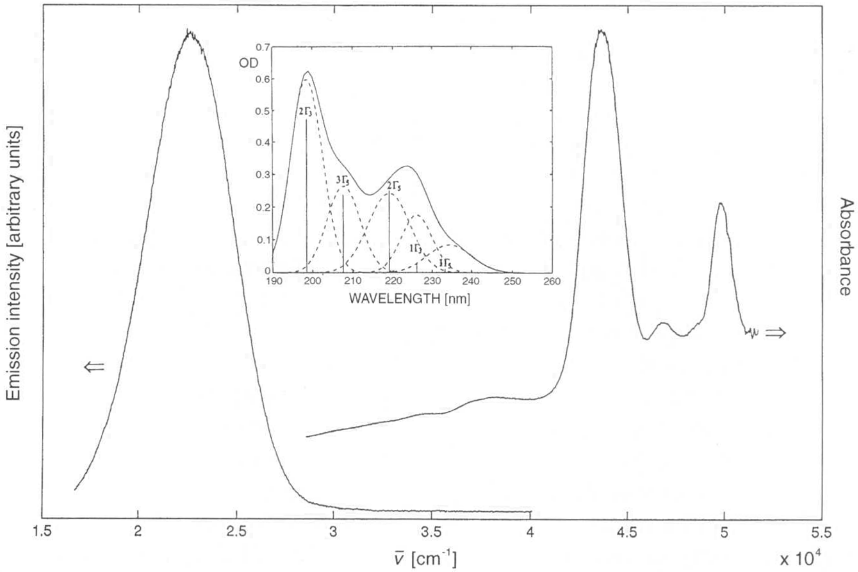

Fig. 2. Absorption and luminescence spectrum of the Ag^+ ion in BaF_2. Shown are the absorption spectrum recorded at 4.2 K and the emission spectrum at 289 K. The surface under the curves decreases above 250 K. Excitation wavelength of the emission is 230 nm. Emission measured by a photon counting system. Absorption measured with a Cary 2300 in absorbance mode. Insert: absorption spectrum of the cubic Ag^+ center in SrF_2 [3].

were obtained with a computer controlled Cary 2300 spectrometer. Polarized and isotropic luminescence spectra were recorded on our laboratory built setup based on a Cary 14/17 monochromator. EPR under uniaxial stress was performed on a computer controlled Varian X-band spectrometer, including a helium dewar and uniaxial stress cavities built in our laboratory. The klystron frequency was always monitored with a Hewlett-Packard microwave frequency counter (type: 5342A) and the magnetic field stabilized with an improved Varian hall stabilizer. An ENDOR attachment [6] and a time domain EPR spectrometer [7] of our construction are further used. The crystals used for the uniaxial stress experiments were slabs of typically $2.8 \times 3.4 \times 8$ mm.

III. Results and discussion

Silver doped BaF_2

The as-grown crystals contain Ag^+ and, in addition, often pairs and clusters. The presence of these latter ones was strongly minimized by selecting care-

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fully the samples within the bulk crystal ingots. These ones exhibit at 4.2 K sample temperature the optical absorption spectrum shown in Fig. 2. It consist of four resolved bands at 49770, 46810, 43610 and 37840 cm^{-1}, with optical density (OD) approximately 15 times higher than the one of the absorption spectrum (insert Fig. 2) of the $SrF_2:Ag^+$ system. Another difference between the two is their respective temperature dependence. The intensity of the absorption spectrum of the $SrF_2:Ag^+$ system increases according to a ctgh(c/T) law whereas the one of $BaF_2:Ag^+$ remains approximately constant below 250 K and decreases up to the highest measured temperature of 400 K. The similarity of the positions of the present absorption bands with those observed for the other alkaline earth fluoride hosts [3] suggests that the four bands arise from the $4d^{10}\ 5d^0 \Leftrightarrow 4d^9\ 5s^1$ transitions of Ag^+. Though the $s-d$ transitions are parity forbidden when the center has inversion symmetry (then the intensity of the absorption signal follows the ctgh(c/T) law) the fact that the present absorption spectrum is of comparatively strong OD and has the temperature dependence as described above, indicate lack of a center of inversion. An emission band peaking at 440 nm of this impurity system was further identified (Fig. 2). Its temperature dependence confirms the absence of an inversion center. Additional information regarding the structure of this Ag^+ center was obtained with the following experiments. The sample was X-rayed typically for 15′ and then spectroscopically investigated. The well-known tetragonal Ag^{2+} EPR spectrum [2] was always observed, often together with the one of a new Ag^0 center. Quantitative correlation between the decrease of the optical absorption spectrum of the Ag^+ impurity and the increase of the EPR spectrum of the Ag^{2+} ion could thereby be established. A detailed ENDOR and time domain EPR study was realized [7, 8] on this last mentioned center to clarify the origin of its tetragonal symmetry. The result is that in addition to the 8 F^- neighbors of the Ag^{2+} ion identified already in [2] an F^- ion is involved actively. It is located in an adjacent fluorine cube in a [001] direction and produces the symmetry lowering. A detailed but standard analysis with the aid of an appropriate spin Hamiltonian [2, 7] allowed to parametrize these spectra. The resulting constants are listed in [2], with the exception, however, of the ones of this F^- ion. These are:

$$A_{\parallel} = 5(5)\ \text{MHz},\ A_{\perp} = 20(1)\ \text{MHz}.$$

Figure 3 presents an ENDOR-induced EPR spectrum of the Ag^{2+} center. This spectrum exhibits particularly clearly the additional components due to the Ag^0 atomic center. A detailed analysis of this latter spectrum was further performed. The result is that this ion has cubic surroundings. Its ground state is an $^2A_{1g}$ state ($5s^1$) resulting in an isotropic g tensor and isotropic hyperfine interaction with the silver nucleus. The EPR spectrum shows both isotopes (^{107}Ag: 51.83%, $g_n = -0.22725$; ^{109}Ag: 48.17%,

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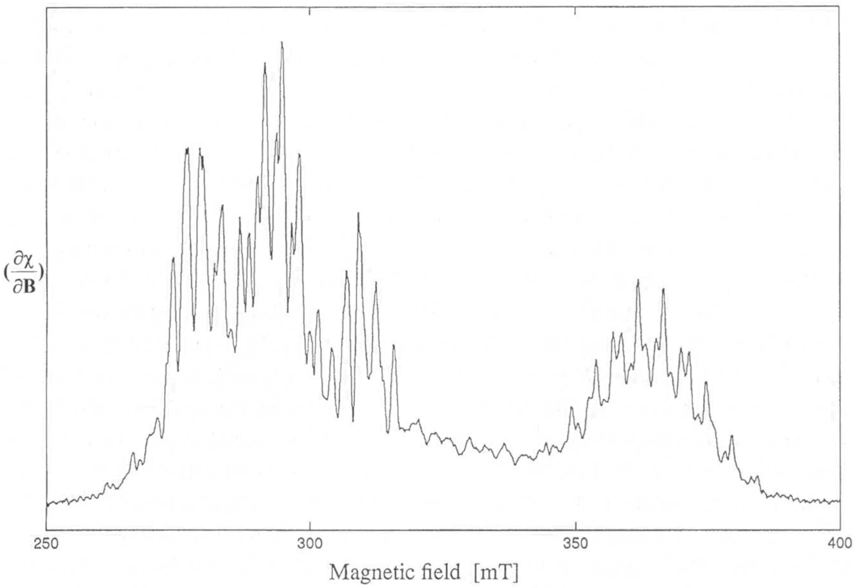

Fig. 3. ENDOR-induced EPR of the Ag^{2+} and the Ag^0 centers in BaF_2. Klystron frequency 9131 MHz. The F^- nuclei were excited. $T = 4.5$ K. $B \| C_3$. On the left the triplet structure of the tetragonal Ag^{2+} spectrum and the low field line group of the silver atom. On the right the high field structure of this latter center. Measured was the first derivative of the susceptibility with respect to the magnetic field **B** as a function of this field. The frequency of the NMR field was always readjusted in order to fulfill the fluorine nuclear Zeeman resonance condition.

$g_n = -0.26174$) resolved. The super hyperfine structure corresponds to 8 equivalent F^- ions, in confirmation of the cubic symmetry of the center. Details will be published elsewhere.

These results show that very likely the Ag^+ ions causing the optical absorption spectrum of Fig. 2 are associated with an F^- ion in an adjacent empty F^- cube along <[001]> and that probably a second Ag^+ center of cubic symmetry exists with a not yet identified absorption spectrum. X irradiation of the crystal produces an electron transfer from the F^- associated silver ion to the one in cubic symmetry. Additionally, this model is supported by the fact that the rather short irradiation time intervals and low doses render improbable the massive and reproducible displacement of lattice or impurity ions. The fact that the intensity of the optical absorption spectrum of the Ag^+ center involving the interstitial fluorine ion decreases with increasing temperature may be explained by a jump diffusion process of the fluorine ion between the six neighboring empty fluorine cubes. When the proccess becomes rapid compared to 1/transition probability of the $s-d$ transitions, it will partially restore the cubic symmetry of the Ag^+ cluster.

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Copper doped CaF_2

The $3d^{10}\,4s^0 \Leftrightarrow 3d^9\,4s^1$ optical absorption spectrum of the Cu^+ ion [5] has an optical density being practically temperature independent between 4.2 K and 280 K but decreasing above this temperature. This shows that this impurity is not exactly located on a host cation lattice site. When CaF_2:copper is X-rays-irradiated the EPR spectrum of the Cu^{2+} center having D_{2h} symmetry [4] emerges. Its increase in intensity correlates with the gradual decrease of the intensity of the $s-d$ transitions of the Cu^+ center. As the EPR results did not allow to decide in an unambiguous way about the model of the Cu^{2+} center we performed EPR under uniaxial stress applied to the crystal. Stress was applied along a C_2 axis (x' in Fig. 1) and EPR spectra were recorded with $B \| C_4$, C_3, C_2' – all being perpendicular to the stress direction (plane ($y'z'$) in Fig. 1). Fig. 4a presents the EPR spectral intensities normalized by the corresponding intensities at no stress in the representation ln(intensity) versus p. Fig. 4b illustrates the results by showing EPR spectra at two different values of p. The stress dependence of the packet labeled g_3 gives highly uncertain results because these lines heavily overlap the spectrum of the Mn^{2+} impurity present in the crystal. For this reason only the results pertaining to the packets g_1, g_2 will be discussed (experiments with other stress orientations are under work). Experiments were performed at temperatures between 4.2 and 23 K. Above ca 25 K the EPR spectrum disappears. The observed strong repopulation effects clearly demonstrate that the six possible orthorhombic orientations of the copper cluster are energetically equivalent and that the system reorients even at low temperature between them. It is enticing to describe this center by a $T_{2g} \otimes (T_{2g} + E_g)$ Jahn-Teller effect, including quadratic coupling terms. Theoretical developments [8, 9] beginning with the pioneering work [10] are available and we draw on these results. In particular [8] has shown that in order to obtain absolute orthorhombic minima in this model it is sufficient to include the quadratic terms transforming as $T_{2g}(E_g \otimes T_{2g})$ into the Jahn-Teller Hamiltonian. The publication [9] establishes criteria for the existence of orthorhombic minima. The adiabatic potential reads

$$\begin{aligned} U = {} & V_E(Q_\theta v_\theta + Q_\varepsilon v_\varepsilon) + V_T(Q_\xi v_\xi + Q_\eta v_\eta + Q_\zeta v_\zeta) + [\omega_E^2(Q_\theta^2 + Q_\varepsilon^2) \\ & + \omega_T^2(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2)] v_A + U_2 + U_S \end{aligned} \tag{1}$$

$$U_2 = V_{TE}^{(2)}\left[\left(\frac{1}{2}Q_\theta - \frac{\sqrt{3}}{2}Q_\varepsilon\right)Q_\xi v_\xi + \left(\frac{1}{2}Q_\theta + \frac{\sqrt{3}}{2}Q_\varepsilon\right)Q_\eta v_\eta - Q_\theta Q_\zeta v_\zeta\right]$$

where U_2 is the quadratic coupling term. U contains the linear JT coupling to an E mode, to a T_2 mode and the elastic energy of both these deformations. The 3×3 matrices v_A.....v_ζ are proportional to the Clebsch-Gordan coefficients within the electronic T_{2g} space and are e.g. defined in [11,

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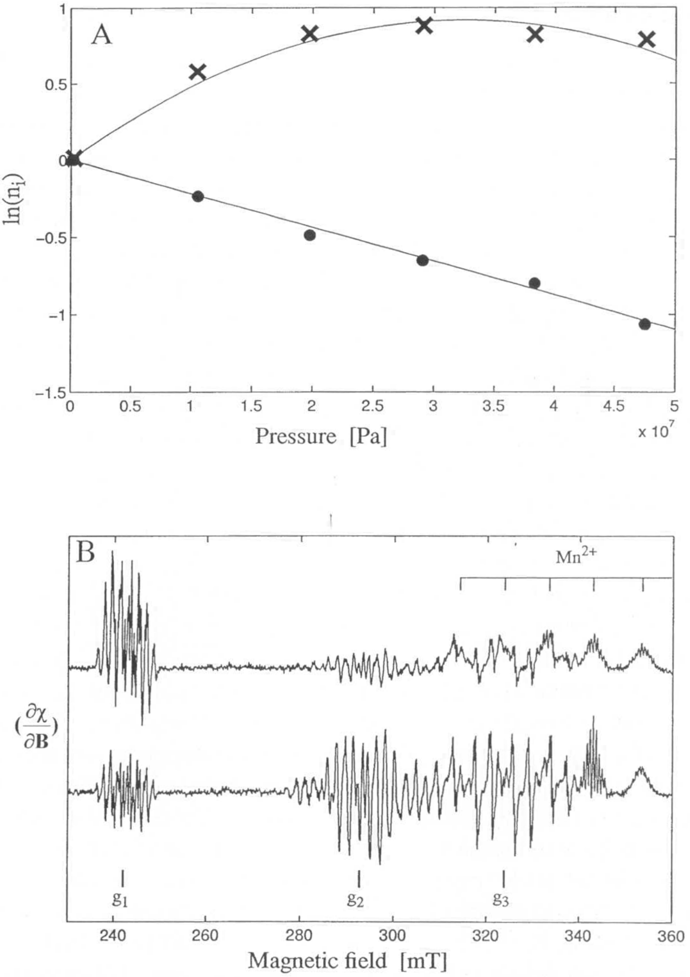

Fig. 4. CaF_2:Cu^{2+} of symmetry D_{2h}. Effect of uniaxial stress, applied along C_2, on the components of the EPR spectrum obtained with $B \| C_2' \perp C_2$. A) The Fig. presents the natural logarithm of the intensity of packet i = 1, 2, normalized by the no-stress value as a function of p. T = 4.2 K. B) EPR spectrum at 0 bar (lower one) and 476 bar, respectively. The center of each packet is specified by ist g value: g_1 = 2.802, g_2 = 2.318, g_3 = 2.103. The ordinate gives the first derivative of the susceptibility as a function of **B**.

Equations 39]. The external stress based on the geometry described above produces the following perturbation Hamiltonian [12]

$$U_s = \left(\frac{V_{ES}}{2}(s_{11}-s_{12})\,v_\theta + \frac{V_{TS}}{2}\,s_{44}v_\zeta\right)\cdot p - \left(\frac{V^{(2)}_{TES}}{2}(s_{11}-s_{12})\,s_{44}v_\zeta\right)\cdot p^2 \tag{1a}$$

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The linear combinations of the T_{2g} basis states associated with the six equivalent minima of Eq. (1) are

$$|\phi_j\rangle = \sum_l c_{lj}|l\rangle \quad \text{with } c_{lj} \quad \begin{array}{rcccc} l= & & \xi & \eta & \zeta \\ j= & 1 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ & 2 & 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ & 3 & 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ & 4 & -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ & 5 & -1/\sqrt{2} & 0 & 1/\sqrt{2} \\ & 6 & 0 & 1/\sqrt{2} & -1/\sqrt{2} \end{array} \qquad (2)$$

$$\varepsilon_j = \frac{V_E^2\omega_T^2 + 4\,V_T^2\omega_E^2 + 2\,V_T V_E V_{TE}^{(2)}}{4(4\omega_E^2\omega_T^2 - V_{TE}^{(2)2})}\,. \qquad (3)$$

The perturbing energy changes due to the applied stress are readily obtained from Eqs. (1a) and (2).

Putting $a = \dfrac{V_{ES}}{8}(s_{11}-s_{12})$, $b = \dfrac{V_{TS}}{2}s_{44}$ and $c = \dfrac{V_{TES}^{(2)}}{4}(s_{11}-s_{12})s_{44}$ one has

$\Delta\varepsilon_1 = (2\cdot a - b)\cdot p + c\cdot p^2$ (packet g_1, Fig. 4)
$\Delta\varepsilon_2 = \Delta\varepsilon_3 = \Delta\varepsilon_5 = \Delta\varepsilon_6 = -a\cdot p$ (3) (packet g_2, Fig. 4)
$\Delta\varepsilon_4 = (2\cdot a + b)\cdot p - c\cdot p^2$ (packet g_3, Fig. 4)

There is good qualitative agreement between the solutions of the model [Eq. (3)] and the experimental stress dependent populations. The packet g_2 exhibits within the error margins a linear stress dependence, whereas the one labeled g_1 clearly involves linear and quadratic contributions. Further, $V_{ES} < 0$, $V_{TS} > 0$. $V_{TES}^{(2)} > 0$, in agreement with the experimental fact that the orbital $|\phi_1\rangle$ is located in the (x', z) plane. This is the preferential orientation of the D_{2h} cluster with respect to the applied stress. The three constants were fitted to the experimental curves. Best agreement was obtained for $\beta\cdot a = -0.219$, $\beta\cdot b = 0.127$ and $\beta\cdot c = 0.087$ with $\beta = 1/(kT)$.

This Cu^{2+} ion is not off-center. It is the only one observed todate by EPR. This model should thus be confronted with the off-center data of [5]. It is very likely that before X-irradiation the copper doped CaF_2 crystals contain this one as Cu^+. The results [5] suggest that this Cu^+ ion is off-center without another impurity being associated.

Conclusions

A detailed optical and paramagnetic resonance study performed on the silver ions in BaF_2 and copper ions in CaF_2 was performed. It allowed to show that BaF_2 contains at least two different Ag^+ centers and that one of these is associated with an interstitial F^- ion whereas the other one is in cubic surroundings. For the first time an Ag^0 atom was observed in BaF_2. With

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the aid of EPR experiments performed under uniaxial stress applied to the sample we showed that the Cu^{2+} ion in CaF_2 of symmetry D_{2h} reorients between 6 equivalent deformations. The results are backed by a theoretical analysis based on the $T_{2g}\otimes(T_{2g}+E_g)$ Jahn-Teller model.

Acknowledgment

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