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Stress-induced orbital alignment of the Cr$^{2+}$ centers in KZnF$_3$ crystal

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Abstract. Observation of the intense linear dichroism spectrum on the $5E_g \rightarrow 5T_{2g}$ transition of Cr$^{2+}$ ions in KZnF$_3$ crystal under uniaxial stress is reported. The model is proposed which assigns the observed spectrum to alignment of the Jahn-Teller Cr$^{2+}$ centers, occurring due to redistribution between the minima of the adiabatic potential that become inequivalent under uniaxial stress applied along the $C_4$ axis of the crystal. Analysis of the observed dependencies of the dichroism on the applied stress has allowed to estimate the values of the electron-strain interaction constant $V_{ES} = 32900 \pm 1200$ cm$^{-1}$ and the inversion splitting $\delta = 9.2 \pm 1.3$ cm$^{-1}$, and also to characterize the random strain field.

1. Introduction
Investigations of the impurity centers with an orbitally-degenerate ground state in the high-symmetry crystals were performed intensely in the second half of the XXth century because of the prediction of the Jahn-Teller effect (JTE) and long-lasting unsuccessful attempts of its experimental observation. Nowadays the interest to such objects is defined by the significant role of the orbital ordering, which occurs due to the cooperative JTE, in formation of the unusual electronic properties of the concentrated transition metal compounds, first of all, oxides. Among those unusual phenomena one finds high-temperature superconductivity in cuprates and colossal magnetoresistance in manganites. Properties of the complex transition metal compounds are defined by numerous degrees of freedom such as charge, orbital, exchange etc. Theoretical understanding of these systems behavior demands the explicit knowledge of the corresponding energy scales. One of the approaches to obtain such information is to study the diluted dielectric crystals. Thus, the double exchange in the Cr$^{2+}$-Cr$^{3+}$ mixed valence pair center has been successfully studied by optical spectroscopy in the KZnF$_3$ crystal doped with chromium ions [1].

It is well known that studies of the impurity centers in the cubic crystals under uniaxial stress can give a lot of information, and, in particular, allow to estimate the vibronic constants [2]. In this paper we present the results of the experimental investigations of the linear dichroism of absorption spectra observed on the $5E_g \rightarrow 5T_{2g}$ transition of the Cr$^{2+}$ ions in KZnF$_3$ crystal. This crystal has a cubic perovskite structure; the symmetry is $Pm\bar{3}m$. Chromium ions substitute for the Zn$^{2+}$ ion sites and are found thus in a sixfold octahedral surrounding of the fluorine ions. Ground state of the Cr$^{2+}$ ions in octahedral surrounding is the $5E_g$ orbital doublet. In such situation the JTE in the strong-coupling limit is expected [3]. It should be mentioned also that the number of publications on the optical spectroscopy of Cr$^{2+}$ ions both in oxide and fluoride compounds is quite small.
In our studies the JT character of the Cr\(^{2+}\) ions ground state is strikingly revealed. The proposed model based on the orbital alignment of the Cr\(^{2+}\) centers under uniaxial stress explains all the experimental observations. It is shown that in order to achieve the quantitative agreement of the model predictions with the experimental data it is necessary to take into account the random strain field.

2. Experimental procedure

The samples of KZnF\(_3\):Cr crystals were grown by Bridgman-Stockbarger method. For doping the CrF\(_2\) compound was used. Concentration of the chromium ions in the samples was in the range of 0.1 – 1.0 wt.% in the charge. It should be mentioned that all the grown crystals except of the doped Cr\(^{2+}\) contained also the Cr\(^{3+}\) ions. Sample orientation along the C\(_4\) crystallographic axis was performed via the cleaved (001) crystal planes. Direction of the C\(_3\) axis was found with the DRON-2M X-ray diffractometer. Accuracy of the orientation was ±2°. Typical size of the sample used in our studies was about 2 × 3 × 6 mm\(^3\). Optical absorption spectra were measured with a single-beam spectrometer based on the DFS-12 monochromator with the Ge-photodiode used as a detector.

Linear dichroism of absorption spectra were registered employing a sensitive differential method proposed in [4]. Light from the output of the monochromator passed through a polarizer and then through a superchromatic plate (SCP) that was adjusted at the 45° angle of its optical axis with respect to the axis of the polarizer. After passing through SCP the light becomes linearly pseudo-depolarized, which means that the intensities of the light with any polarization are equal. Rotation of the analyzer placed after SCP leads in the case of the absorption anisotropy in the sample to the intensity modulation of the light transmitted through the sample. Detected signal then would contain the component at the frequency twice that of the analyzer rotation with an amplitude proportional to the linear dichroism. Dichroism value was defined as

\[
D = \frac{I_\parallel(\lambda) - I_\perp(\lambda)}{I_\parallel(\lambda) + I_\perp(\lambda)}
\]

and was calculated using the measured dichroism signal \((I_\parallel(\lambda) - I_\perp(\lambda))\) and the intensity of the light passed through the sample at zero pressure \(I_0(\lambda)\) that were measured keeping all the other experimental conditions identical:

\[
D = \frac{I_\parallel(\lambda) - I_\perp(\lambda)}{2I_0(\lambda)}.
\]

Expression (2) is valid if the dichroism is small. Also, if the absorption is weak then the last expression can be rewritten as

\[
D = \frac{k_\parallel(\lambda) - k_\perp(\lambda)}{2},
\]

where \(k_\parallel(\lambda)\) and \(k_\perp(\lambda)\) are the absorption coefficients. Investigations were performed in the bath cryostat. Uniaxial strain was created with a pneumatic press, uniaxial stress on the sample had the values up to 100 MPa. Strain magnitudes were calculated using the components of the compliance tensor \(S_{11} = 0.821 \times 10^{-12} \text{cm}^2/\text{dyn}\) and \(S_{12} = -0.204 \times 10^{-12} \text{cm}^2/\text{dyn}\) [5]. Relative strain value of the \(E_\theta\) symmetry is \(\epsilon_0 = (S_{11} - S_{12})/P\), where \(P\) is the stress applied along the C\(_4\) axis.

3. Experimental results

Optical absorption and linear dichroism spectra measured at \(T = 4.2\ \text{K}\) with stress applied along the C\(_4\) and C\(_3\) axes of the crystal are shown in figure 1. Absorption band with the maximum at 820 nm has a weakly pronounced structure and corresponds to the \(^5E_g \rightarrow ^5T_{2g}\) transition of the Cr\(^{2+}\) ion. Two narrow zero-phonon lines are observed at the long-wavelength wing of the band. Another wide band with a pronounced structure that has a maximum at 670 nm originates from Cr\(^{3+}\) ions and is assigned to the \(^4A_{2g} \rightarrow ^4T_{2g}\) transition. When the uniaxial stress is applied along the C\(_4\) principal axis of the crystal the
intense linear dichroism signal is observed within the range of the wide vibronic absorption band of the Cr$^{2+}$ ions (figure 1). When the stress of the same value is applied along the C$_3$ axis, no dichroism signal was found.

**Figure 1.** Absorption (a) and the linear dichroism spectra under the stress applied along the C$_4$ (b) and C$_3$ (c) axes of the KZnF$_3$:Cr crystal; T = 4.2 K, P = 64 MPa. In the inset the energy level diagram of the Cr$^{2+}$ ion in the crystal field of D$_{4h}$ symmetry and the transition polarizations from the ground $^3$B$_{1g}$ state are shown.

The shape of the dichroism signal within the wide vibronic band is not modified with the stress value variation. Dependencies of the dichroism signal amplitude on stress at $\lambda = 800$ nm are shown in figure 2. Dependencies on stress measured at different wavelengths within the absorption band of the Cr$^{2+}$ ions at a given temperature have the identical character and differ only in the magnitude.

### 4. Physical model

Let us consider now the origin of the observed phenomenon. Magnitude of the dichroism signal which is of the same order as the absorption coefficient of the Cr$^{2+}$ ions indicates that an essential fraction of the Cr$^{2+}$ ions is involved. In our opinion, nature of the dichroism signal under uniaxial stress is closely related to the JTE. The ground $^3E_g ($$^3e_g$) state of the Cr$^{2+}$ ions interacts strongly with the nearest surrounding distortions of the $E_g$ symmetry. Such [CrF$_6$]$^{4-}$ cluster distortions are described usually by the two normal modes $Q_\theta$ and $Q_\epsilon$ that transform as $(3z^2-r^2)$ and $(x^2-y^2)$, respectively [3]. These modes can be expressed also as $Q_\theta = \rho \cos \phi$ and $Q_\epsilon = \rho \sin \phi$, where $\phi$ is a polar angle in the $(Q_\theta, Q_\epsilon)$ plane counted from the $Q_\theta$ axis. The $E \otimes e$ JT problem solution is well known. Account for the linear and the third order ($\propto \rho^3$) terms in the Hamiltonian leads to the adiabatic potential (AP) with the three equivalent minima that correspond to either elongated or compressed along the three C$_4$ cluster axes. At low temperatures, the particles are localized in the vicinity of the minima, where the system states are described by the vibronic wavefunctions of $\Phi_i = \psi_- \Psi_i (\rho, \phi), i = X, Y, Z$, where $\psi_-$ is an electronic wavefunction of the lower sheet of AP and $\Psi_i (\rho, \phi)$ is a vibrational wavefunction localized nearby the points of $\rho = \rho_0$, $\phi = \phi_{\text{min}}$ [3]. If the height of the barriers between the minima is finite, a tunneling occurs that significantly modifies the energy spectrum of the system: the three lowest levels are represented by the vibronic doublet $E_g$ and the singlet $A_1$ (or $A_2$). Singlet is higher in
energy than the doublet by an interval of \( \delta \) which is called the inversion (or tunneling) splitting [3].

Wavefunctions of the singlet and the doublet in the case of the elongated cluster configurations in the minima of AP are described by the linear combinations

\[
|A_1\rangle = \frac{1}{\sqrt{3}} (\Phi_x + \Phi_y + \Phi_z), \\
|E\theta\rangle = \frac{1}{\sqrt{6}} (2\Phi_z - \Phi_x - \Phi_y), \\
|E\epsilon\rangle = \frac{1}{\sqrt{2}} (\Phi_x - \Phi_y),
\]

where \( \Phi_i \) are the vibronic states that correspond to the AP minima [3].

![Figure 2](image-url)

**Figure 2.** Dependencies of the dichroism signal on stress at the temperatures of 2.0 K, 4.2 K and 77 K, \( \lambda = 800 \) nm, \( P\parallel C_4 \). Symbols indicate the experimental data, the lines are the results of the fits: dashed lines – with the use of distribution (9), solid lines – (10). Corresponding random strain distributions are also shown.

Hamiltonian of the system that accounts for the interaction with the \( E_g \)-symmetry distortions (described by the \( c_\theta \) and \( c_\epsilon \) components of the strain) in the basis (4) has the form:

\[
H = H_0 + H_{ES} = \begin{pmatrix}
\delta & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix} + \begin{pmatrix}
0 & rV_{ES}c_\theta & rV_{ES}c_\epsilon \\
rV_{ES}c_\theta & -qV_{ES}c_\theta & qV_{ES}c_\epsilon \\
rV_{ES}c_\epsilon & qV_{ES}c_\epsilon & qV_{ES}c_\theta
\end{pmatrix},
\]

where \( q \) and \( r \) are the matrix elements of the type \( q = \langle Ec_\theta | U_\theta | E\epsilon \rangle = -\langle E\theta | U_\theta | E\epsilon \rangle = \ldots \) and \( r = \langle A_1 | U_\epsilon | E\epsilon \rangle = \langle A_1 | U_\theta | E\theta \rangle \), \( V_{ES} \) is an electron-strain interaction constant.

Under the uniaxial stress applied along the \( C_4 \) axis of the crystal, the ensemble of the JT centers becomes at low temperatures essentially anisotropic due to the redistribution of the centers between the inequivalent energy minima. As a consequence, the optical spectra of such system become anisotropic with respect to the direction of the applied stress (\( E \parallel P \) and \( E \perp P \)). In our opinion,
exactly the described situation causes the intense linear dichroism observation within the absorption band of the Cr$^{2+}$ ions in KZnF$_3$ crystal.

In the AP minima the [CrF$_6$]$^{4–}$ cluster has the tetragonal symmetry. The corresponding energy level pattern is shown in the inset of Fig. 1. Orthogonally polarized transitions from the ground $^3$B$_1g$ state to the $^3$E$_g$ and $^3$B$_2g$ sublevels of the excited $^5$T$_2g$ state explain naturally the observed dichroism spectrum structure. Our hypothesis explains also a zero dichroism signal under the stress applied along the C$_3$ crystalline axis: interaction with such deformation leaves the AP minima equivalent.

The problem of the center redistribution between the AP minima as a function of the applied stress value and the temperature in the case of $P \square C_4$ can be solved analytically. Let the stress be applied along the z-axis and the light propagates along x. We assume also that the light absorption is caused by the electric-dipole transitions and an applied stress does not modify the electronic wavefunctions of the initial and the final states. Then the dichroism signal within the absorption band will be proportional to

$$D \propto \frac{N_z - N_y}{N_x + N_y + N_z},$$  \hspace{1cm} (6)$$
where $N_i$ are the populations of the corresponding vibronic states $\Phi_i$. Taking into account the Boltzmann distribution between the energy levels and knowledge of the eigenvectors of the Hamiltonian (5) together with the expressions for the wavefunctions (4) allows to derive the populations of the minima corresponding to $\Phi_X$, $\Phi_Y$ and $\Phi_Z$ states. As a result, the following expression has been obtained:

$$D \propto \frac{\exp\left(\frac{3\xi - 1}{\tau}\right)\left[\cosh\left(\frac{\Omega}{\tau}\right) + x\left(1 - 4\sqrt{2a}\right)\sinh\left(\frac{\Omega}{\tau}\right)\right]}{2\exp\left(\frac{3\xi - 1}{\tau}\right)\cosh\left(\frac{\Omega}{\tau}\right) + 1},$$  \hspace{1cm} (7)$$
where we introduce the dimensionless parameters $\xi = qV_{Eg}c_q / \delta$, $\tau = 2k_BT / \delta$, $\Omega = \sqrt{(4a^2 + 1)c_q^2 + 2c_q + 1}$, $a = r / q$.

The curves $D(\xi, \tau)$, calculated using expression (6), reproduce qualitatively the experimental data. Moreover, each of the dependencies, measured at 2 K and 4.2 K, can be almost ideally fit with (6). However, it has turned out that these two dependencies cannot be fit within the proposed model simultaneously, with the same set of the parameters. Obviously, some additional factors should be taken into account.

One of such factors that had to be accounted for in the majority of the JTE experimental studies is the random strain field present in any real crystal. As we study the cubic symmetry crystal, due both to the orientation degeneracy and the averaging in time between the three axial configurations of the [CrF$_6$]$^{4–}$ cluster related to the tunneling of each center through the barriers, the dichroism signal is absent at zero applied stress. Random strains also should not violate the high cubic symmetry of the problem. This is why the E$_g$-symmetry strains were taken as $c_{hh} = c_s \cos \varphi$ and $c_{ss} = c_s \sin \varphi$ with the homogeneous distribution over $\varphi$ in the range of $0...2\pi$ and some distribution $f(c_s)$ that has a maximum at $c_s = 0$ and drops gradually with $c_s$ increase. When a nonzero stress was applied along the C$_4$ axis of the crystal, the distortions originating from the random strains and from an applied stress were considered additive. Averaging over the random strain distribution was performed numerically, via evaluation of the integral.

$$\int_{0}^{2\pi} f(c_s) \cos \varphi \, d\varphi = \frac{1}{2}.$$  

$$\int_{0}^{2\pi} f(c_s) \sin \varphi \, d\varphi = 0.$$  

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\[
\langle D(T, c_\phi) \rangle = \frac{1}{2\pi} \int_0^{2\pi} d\varphi \int_0^\infty c_\phi D(T, c_\phi + c_\theta, c_\delta) f(c_\delta) dc_\delta.
\] (8)

Here, the function of \( D(T, c_\phi, c_\delta) \) was defined by (5). The fit of the measured dependencies of the dichroism signal on stress value was performed within an assumption that the JTE in the ground \(^5\text{E}_g\) state of the Cr\(^{2+}\) ions in KZnF\(_3\) crystal is realized in the strong coupling limit \((q = 0.5, r = -\sqrt{2})\).

Parameters varied during the fitting procedure were \(V_{ES}, \delta\), the width of the random strain distribution \(w\) and the amplitude.

As far as the shape of the distribution \(f(c_\delta)\) is concerned, the regularly used one is the Gaussian

\[
f(c_\delta) = \frac{1}{\sqrt{\pi w^2}} \exp\left(-\frac{c_\delta^2}{w^2}\right).
\] (9)

Indeed, from the point of view of the random strain impact modeling, distribution (9) is very nice: it has the steeply vanishing wings \((\propto e^{-x^2})\) and the averaging procedure is performed with no problem. However, physically, following [6, 7], random strains are described by (9) if it originate from the dislocations in the crystal. Otherwise, if random strains occur due to the point defects, the distribution is different [7]:

\[
f(c_\delta) = \frac{A}{(c_\delta^2 + w^2)^{\frac{3}{2}}}.
\] (10)

where \(A\) is a normalizing factor.

We have studied both distributions. Results of the simultaneous fits of the dichroism signal dependencies on the applied stress at 2 K, 4.2 K and 77 K are shown in figure 2 and in Table 1. Both in the figure (visually) and from the table data \((\chi^2\) differs by almost an order of magnitude) it is clearly seen that the use of distribution (10) allows for a much better reproduction of the experimental data. This, in our opinion, indicates unambiguously that the random strain field in the studied sample originates predominantly from the point defects in the crystal.

**Table 1.** Parameters of the dichroism signal stress dependencies fit obtained with an account of the random strains in the crystal described by the distributions (9) and (10).

| Random strain distribution | \(V_{ES}\) (cm\(^{-1}\)) | \(\delta\) (cm\(^{-1}\)) | \(w\) | \(\chi^2\) |
|----------------------------|----------------|----------------|------|--------|
| Gaussian, equation (9)     | 33600±1600     | 13±2           | (1.44±0.15)\(\times\)\(10^{-4}\) | 0.0106 |
| Equation (10)              | 32900±1200     | 9.2±1.3        | (6.9±0.9)\(\times\)\(10^{-5}\)  | 0.0027 |

Thus, we see that an account for the random strains that are inevitably present in the crystal has allowed to fit nicely all the experimental data. Importantly, the kind of experiments we perform is sensitive to the shape of the random strain distribution and such studies are capable to provide one with an additional, both **qualitative and quantitative**, information about the defects in the crystal. It should be mentioned also that the parameter values presented in Table 1 differ for two types of the random strain distributions just slightly, by ~30% maximum, and thus do not depend critically on the shape of the distribution employed.
The width of the random strain distribution is \( w = 6.9 \times 10^{-5} \) in the relative strain units, which corresponds to the average value of the \( \text{Cr}^{2+} \) ion interaction with random strains of \( qV_{ES}w = 1.1 \text{ cm}^{-1} \). The linear JT constant \( V \) is related in the case of a 6-fold coordination to \( V_{ES} \) by \( V = \frac{3V_{ES}}{2R} \), where \( R \) is a distance to the nearest neighbor, \( R = \frac{a}{2} \), and \( a = 4.055 \text{ Å} \) is the KZnF$_3$ crystal lattice constant. This gives an estimate of \( V \approx 1.7 \text{ eV/Å} \).

6. Conclusions
In summary, we relate an observed at low temperatures intense linear dichroism signal within wide absorption band of the \( \text{Cr}^{2+} \) ions in KZnF$_3$ crystal under uniaxial stress applied along the C$_4$ axis of the crystal to the orbital alignment of the \( \text{Cr}^{2+} \) Jahn-Teller centers. Or, equivalently, the centers are redistributed between the minima of the adiabatic potential that become inequivalent under a stress applied along the C$_4$ direction. Analysis of the measured dependencies of the dichroism signal on stress allowed to define the values of the electron-strain interaction constant \( V_{ES} = 32900 \pm 1200 \text{ cm}^{-1} \), the inversion splitting \( \delta = 9.2 \pm 1.3 \text{ cm}^{-1} \) and the width of the random strain distribution \( w = (6.9 \pm 0.9) \times 10^{-5} \). Our experiments were found to be sensitive to the shape of the random strain distribution and thus allow to reveal the essential origin of the random strains in the sample.

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