Optical studies of Cr$^{3+}$-Cr$^{2+}$ pair center in KZnF$_3$ crystal

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Abstract

Optical absorption spectra of Cr$^{3+}$-Cr$^{2+}$ pair center in KZnF$_3$:Cr$^{3+}$,Cr$^{2+}$ crystal were investigated in wide temperature range. Broad band at 30800 cm$^{-1}$ is attributed to cation-cation $e_g$-electron transfer transition. Narrow lines with maxima at 16720 cm$^{-1}$ and 19880 cm$^{-1}$ have been assigned to purely electronic exchange-induced electric-dipole transitions from the ground (Cr$^{3+}$,4$^4A_2g;Cr^{2+}$,5$^5E_g$) state to excited (Cr$^{3+}$,4$^4A_2g;Cr^{2+}$,3$^3E_a$) and (Cr$^{3+}$,4$^4A_2g;Cr^{2+}$,3$^3E_b$) states, respectively. It’s vibronic satellites corresponding to $a_{1g}$ local mode of Cr$^{3+}$ fluorine octahedron of the pair are also observed. Energy of the local mode for the ground and mentioned excited states are 580, 540 and 530 cm$^{-1}$. Instead of expected double exchange for mixed valence pair ferromagnetic superexchange for Cr$^{3+}$-Cr$^{2+}$ pair in KZnF$_3$ crystal is realized. Exchange integral $J$ = $-14.9 \pm 0.4$ cm$^{-1}$ and Jahn-Teller splitting $\Delta_{JT} = 340 \pm 40$ cm$^{-1}$ for the ground state of the pair were obtained by analysis of the temperature dependence of absorption lines. Important features of the crossover double exchange - ferromagnetic superexchange are discussed.

Key words: D. Exchange and superexchange, D. Valence fluctuations, D. Electronic states (localized). E. Light absorption and reflection

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1 Introduction

Investigations of dynamic charge fluctuations in compounds like $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{NaV}_2\text{O}_5$, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ are in the focus of condensed matter physics. Physical essence of charge-spin dynamics in these systems in our opinion can be revealed to some extent by investigations of simple model mixed valence systems containing small number of ions, the Hamiltonian of which may be solved exactly. For example in the small polaron theory [1,2] undoubtedly having relationship to this problem main characteristics are introduced in the two-site model.

In [3–5] we have reported the observation of the optical absorption lines of $\text{Cr}^{3+}$-$\text{Cr}^{2+}$ mixed valence pair center in $\text{KZnF}_3:\text{Cr}^{3+},\text{Cr}^{2+}$ crystals (Fig.1,a). Optical piezospectroscopy investigations have shown that symmetry of the pair is tetragonal. The most plausible model is that chromium ions are located in neighboring sites along $C_4$-axis of crystal. Observation of linear Stark effect on the absorption lines of $\text{Cr}^{3+}$-$\text{Cr}^{2+}$ pair [5] yields evidence that the pair doesn’t have center of symmetry at studied time scale.

In this paper we report the energy level structure of the ground state of the pair. Several important characteristics as exchange integral, energy of $e_g$-electron localization, frequencies of local lattice vibrations near the pair center have been obtained. We also point out important features of the crossover double exchange - ferromagnetic superexchange in the ground state of $\text{Cr}^{3+}$-$\text{Cr}^{2+}$ pair.

2 Results and discussion

Symmetry of $\text{KZnF}_3$ crystals is $Pm\bar{3}m$, lattice constant is $a=4.055$ Å. The samples were grown by Bridgman-Stockbarger method, for crystals doping $\text{CrF}_3$ and $\text{CrF}_2$ compounds were used. The concentrations of chromium ions were varied in the range $0.1\div2$ wt.%. The concentrations of $\text{Cr}^{3+}$ and $\text{Cr}^{2+}$ ions in crystals were determined by measuring of absorption coefficients of the bands corresponding to $^4A_{2g} \rightarrow ^4T_{2g}$ (14930 cm$^{-1}$) and $^5E_g \rightarrow ^5T_{2g}$ (11900 cm$^{-1}$) transitions of single ions, respectively.

Absorption spectra were measured on the Specord-M40 spectrophotometer. For investigations of absorption spectra in temperature range $4.2\div300$ K Oxford Instruments CF-1204 optical cryostat was used.

Absorption spectrum of $\text{KZnF}_3:\text{Cr}^{3+},\text{Cr}^{2+}$ crystal with dopant’s concentrations $n(\text{Cr}^{3+})=1.8\cdot10^{18}$ cm$^{-3}$ and $n(\text{Cr}^{2+})=9.2\cdot10^{18}$ cm$^{-3}$ is presented in
Fig. 2, a. On the wing of very intense band at $>50000 \text{ cm}^{-1}$ a wide band at $\sim 43000 \text{ cm}^{-1}$ with the halfwidth $\sim 7000 \text{ cm}^{-1}$ is observed. Studies of crystals containing various concentrations of Cr$^{3+}$ and Cr$^{2+}$ ions have displayed that intensities of these bands depend on concentration of Cr$^{2+}$ ions only. Absorption bands observed at 59000 cm$^{-1}$ and 46300 cm$^{-1}$ in the spectrum of KMgF$_3$:Cr$^{2+}$ crystal were assigned to transitions from 3$d$ to 4$p$ and 4$s$ states of Cr$^{2+}$ ions, respectively [6, 7]. Since KMgF$_3$ crystal is isostructural to KZnF$_3$ it is natural to conclude that absorption bands of KZnF$_3$:Cr$^{3+}$,Cr$^{2+}$ crystal at $>50000 \text{ cm}^{-1}$ and $\sim 43000 \text{ cm}^{-1}$ should be attributed to 3$d$→4$p$ and 3$d$→4$s$ transitions of single Cr$^{2+}$ ions, respectively.

In crystals with bigger concentrations of Cr$^{3+}$ ions (absorption spectrum of a sample with $n(\text{Cr}^{3+})=1.3 \cdot 10^{20} \text{ cm}^{-3}$ and $n(\text{Cr}^{2+})=7.3 \cdot 10^{18} \text{ cm}^{-3}$ is shown in Fig. 2, b) additional absorption band at 30800 cm$^{-1}$ with the halfwidth $\sim 7000 \text{ cm}^{-1}$ (except of well known $d$→$d$ transitions of single Cr$^{3+}$ ions [8]) has been observed. Intensity of this band correlates to intensities of absorption lines of Cr$^{3+}$-Cr$^{2+}$ pair center in the visible (Fig. 1, a). Its oscillator strength to our estimates is $f \sim 10^{-1}$. These facts allowed us to assign absorption band with $\nu_{\text{max}} \sim 30800 \text{ cm}^{-1}$ to charge-transfer transition $(\text{Cr}^{2+}, t^3_{2g}, e_g : \tilde{5}E_g; \text{Cr}^{3+}, t^3_{2g} : 4A_2g \rightarrow (\text{Cr}^{3+}, t^3_{2g} : 4A_2g; \text{Cr}^{2+}, t^3_{2g}, e_g : \tilde{5}E_g)$ of Cr$^{3+}$-Cr$^{2+}$ pair center.

High energy of this transition reveals strong interaction of the pair center with the lattice. Indeed, let us consider the small polaron two-site model [1, 2] taking into account the appropriate electronic states of Cr$^{3+}$ and Cr$^{2+}$ ions. Hamiltonian of the system in the second quantization form is written as:

$$\hat{H} = \frac{p^2}{M} + \frac{M \omega^2}{2}q^2 + Vq(a^+a - b^+b) + t(a^+b + b^+a),$$

(1)

where $q$ is a vibrational coordinate describing the difference in local surrounding displacements corresponding to the localization of ”extra” $e_g$-electron at a or b Cr$^{3+}$ ion:

$$q = Q_a - Q_b,$$

(2)

$p$ - momentum canonically conjugated to coordinate $q$; $V$ is a parameter of linear vibronic interaction with $Q_a$ and $Q_b$ modes of fluorine octahedra of a and b ions; $a$, $a^+$, $b$, $b^+$ - creation and annihilation operators of $e_g$-electron at ions a and b, respectively; $t$ is a transfer integral.

In the case $q=0$, Hamiltonian (1) corresponds to usual double exchange, it’s diagonalization was described in [9]. Energy level scheme of the system depends on total spin of the pair and is equidistant:

$$\varepsilon(S) = \pm t(S + \frac{1}{2}),$$

(3)
where \( \tilde{t} = t/(2S_0 + 1) \), \( S_0 \) is ion core spin. In our case the ion core is \((t_{2g}^3 : A_2g)\) and \( S_0 = 3/2 \).

For \( q \neq 0 \), diagonalization of (1) gives the following expression for adiabatic potentials:

\[
E^\pm(q, S_0) = \frac{M\omega^2 q^2}{4} \pm \sqrt{\frac{V^2 q^2}{4} + \varepsilon^2(S_0)}. \tag{4}
\]

As one can see, when \( \varepsilon(S) \gg Vq \) the adiabatic potential has a minimum at \( q = 0 \). This case corresponds to modified double exchange, the energy spectrum is still equidistant. If the vibronic energy is larger than \( \varepsilon(S) \) the adiabatic potential has two wells as it is shown in Fig.3 (vertical arrow indicates possible charge-transfer transition). This case corresponds to partial localization of "extra" \( e_g \)-electron at a or b centers. For adiabatic potential in Fig.3 the following set of parameters was used: the transfer integral between \((3z^2 - r^2)\) orbitals via intermediate fluorine ion \( t_{uu} = 2400 \text{ cm}^{-1} \) as it is found in [10] from analysis of the optical spectra of exchange-coupled Cu\(^{2+}\)-Mn\(^{2+}\) pairs in KZnF\(_3\) crystal, \( V \) was obtained from the energy of charge-transfer transition \( Vq_0 = 30800 \text{ cm}^{-1} \), where \( q_0 \) is equilibrium coordinate, \( \hbar\omega = 580 \text{ cm}^{-1} \) and will be explained below.

In the minima of adiabatic potentials \( e_g \)-electron is mainly localized at one of the ions of the pair. Energy spectrum corresponding to minima of adiabatic potentials obeys Lande intervals rule

\[
E^-(q_0, S) - E^-(q_0, S - 1) \approx -\frac{2\tilde{t}^2}{Vq_0} S, \tag{5}
\]

and hence can be described as superexchange.

We can say that electron-lattice interaction suppresses double exchange modifying it to ferromagnetic superexchange. As it can be easily seen from (4), crossover double exchange - ferromagnetic superexchange happens rather sharply with vibronic coupling increase. These features of crossover haven’t been mentioned in literature before but are very important in our opinion.

The intensities of absorption lines 1 \((\nu_{max} = 16720 \text{ cm}^{-1}, \text{ Fig.1})\), 2 \((19880)\), 1’ \((17260)\), 2’ \((20410)\), 1” \((16140)\) and 2” \((19300)\) are proportional to the product of Cr\(^{3+}\) and Cr\(^{2+}\) ions concentrations and therefore these lines were assigned to Cr\(^{3+}\)-Cr\(^{2+}\) pair center [3]. The estimate of oscillator strengths of lines 1 and 2 as \( f \sim 5 \cdot 10^{-4} \) shows that these lines can be attributed to electric-dipole transitions. Analysis of exchange-induced electric-dipole transitions of Cr\(^{3+}\)-Cr\(^{2+}\) pair center\(^2\) including relative intensities and selection

\(^2\) Detailed analysis of transitions exceeds the limits of present work and will be reported elsewhere [11]
rules according to [12] permits us to unambiguously assign lines 1 and 2 to purely electronic transitions from the ground \((\text{Cr}^{3+}:^4\text{A}_2\text{g}; \text{Cr}^{2+}:^5\text{E}_g)\) to excited \((\text{Cr}^{3+}:^4\text{A}_2\text{g}; \text{Cr}^{2+}:^3\text{E}_g)\) and \((\text{Cr}^{3+}:^4\text{A}_2\text{g}; \text{Cr}^{2+}:^3\text{E}_a\text{g})\) states, respectively. These excited states have nearly the same electronic configurations \((\text{Cr}^{3+}:^3\text{E}_g; \text{Cr}^{2+}:^3\text{E}_a\text{g})\) as the ground state, total spin is changed only. As a consequence the adiabatic potentials of the ground and given excited states are almost identical. In this way we explain why the absorption lines 1 and 2 are narrow.

Lines 1' and 2' are observed in the spectrum equal energy intervals apart from lines 1 and 2. Their temperature dependencies are within a constant factor the same as those for lines 1 and 2 (Fig.4). To the lower energies from absorption lines 1 and 2 lines 1'' and 2'' clearly displayed in the derivative of absorption spectrum (Fig.1, b) at \(T= 300\) K are observed. These lines disappear when temperature is lowered to \(T\sim 150\) K (Fig.1, c) and therefore can be assigned to transitions including excited vibronic states. Lines 1' and 2' correspond to transitions with \(\Delta n = 1\), where \(n\) is vibrational quantum number, lines 1'' and 2'' - to transitions with \(\Delta n = -1\). Energies of vibronic modes for the ground and the excited states can be easily determined from spectrum and are equal to \(\hbar \omega_g=580\pm 20\) cm\(^{-1}\), \(\hbar \omega_1=540\pm 20\) cm\(^{-1}\) and \(\hbar \omega_2=530\pm 20\) cm\(^{-1}\), respectively. It is interesting to point that \(\hbar \omega_g\) is equal to the energy of local vibration mode of \(a_{1g}\) symmetry as it is reported for single Cr\(^{3+}\) ion in KZnF\(_3\) crystal (574 cm\(^{-1}\), [13]). This fact allows us to conclude that \(Q_a\) and \(Q_b\) in (2) are mainly "breathing" modes of the fluorine octahedra near the ions of the pair. It should be mentioned that condensation of local vibration due to localization of extra charge on the lattice site was expected and discussed in theory (see for example [2]), but to our knowledge we report here their so clear experimental observation for the first time.

Intensities of absorption lines 1, 2, 1' and 2' depend strongly on temperature. They are not observable at \(T<15\) K. When temperature increases intensities of these lines grow, show up a maximum at \(T\sim 150\) K and decrease slowly with further temperature increase (Fig.4). Strong temperature dependence of absorption lines of Cr\(^{3+}-\text{Cr}^{2+}\) pair center in the temperature range \(T<120\) K can be naturally explained by ferromagnetic type of exchange interaction in the ground state. In this case total spin state with \(S=\frac{7}{2}\) is the ground state. Electric-dipole transitions from this sublevel obeying the selection rule \(\Delta S = 0\) are forbidden because in excited states \((\text{Cr}^{3+}:^4\text{A}_2\text{g}; \text{Cr}^{2+}:^3\text{E}^{a,b}_g)\) of the pair states with \(S=\frac{7}{2}\) are absent. Absorption appears due to thermal occupation of the excited states with \(S=\frac{5}{2}, \frac{3}{2}\) and \(\frac{1}{2}\).

The quantitative analysis of temperature dependence of absorption lines was successfully performed under following conclusions. The localization energy (or polaronic shift) \(V q_0/4 \sim 7700\) cm\(^{-1}\) is large enough with respect to \(e_g\)-electron transfer energy and as a result we have the case of ferromagnetic superexchange instead of expected double exchange. This conclusion is supported by
the observation in absorption spectrum of vibronic satellites. Transitions from excited vibronic sublevel were also taken into account. Parameters $V q_0$ and $t_{uu}$ for this state were taken the same as for the ground vibronic state. The splittings of the ground state spin multiplets $S = \frac{7}{2}$, $S = \frac{5}{2}$ and $S = \frac{3}{2}$ due to spin-orbit interaction and axial component of crystal field are small in respect to exchange splittings [11] and were neglected. Relative probabilities of transitions from different total spin states were found in [3]:

$$W(\frac{5}{2}) : W(\frac{3}{2}) : W(\frac{1}{2}) = 21 : 16 : 5.$$  \hspace{1cm} (6)

Result of the fit within the proposed model is shown in Fig.4 by dashed line. For the temperature range $T < 120$ K observed temperature dependence is fairly well fitted, but at higher temperatures significant disagreement appears. This disagreement hints at the importance of Jahn-Teller nature of $[CrF_6]^{4-}$ fragment of the pair center, which was not treated here up to now. Due to the presence of $Cr^{3+}$ ion in the pair center three minima of adiabatic potential of $[CrF_6]^{4-}$ cluster have different energies. Minimum corresponding to elongation of the octahedron towards $Cr^{3+}$ ion is the deepest, $e_g$-electron resides at $(3z^2 - r^2)$ orbital. Other two minima which correspond to perpendicular elongations of fluorine octahedron are equivalent and a little bit higher in energy (energy gap between the minima is $\Delta_{JT}$). It is obvious that the transfer integral between $(3x^2 - r^2)$ and $(3y^2 - r^2)$ orbitals of chromium ions due to their small overlapping with $p$-orbitals of intermediate $F^-$ ion will be much smaller than that for $(3z^2 - r^2)$ orbital. For this reason exchange splitting of these Jahn-Teller states will be relatively small. Since $e_g - e_g$ kinetic exchange is the main mechanism of the exchange-induced optical absorption, it is clear that described Jahn-Teller excited states do not contribute to absorption spectrum. The excited state at energy $\Delta_{JT}$ is forty-fold degenerate. It’s thermal occupation yields to the drop of absorption lines intensities at $T > 150$ K.

Final fit of the temperature dependence including Jahn-Teller states as considered above is shown in Fig.4 by solid line. The values of extracted parameters are: $J = -14.9 \pm 0.4$ cm$^{-1}$, $\Delta_{JT} = 340 \pm 40$ cm$^{-1}$. As one can see, fitting curve fairly well follows experimental dependence in the whole temperature range.

3 Summary

Main results of the paper can be summarized as follows. Absorption band with $\nu_{max} \sim 30800$ cm$^{-1}$ in KZnF$_3$:Cr$^{3+}$,Cr$^{2+}$ crystal spectrum corresponds to cation-cation charge-transfer transition from Cr$^{2+}$ ion to Cr$^{3+}$. Large charge-transfer energy reveals high degree of extra charge localization at one of the ions of the pair caused by strong vibronic interaction. Energy of charge localization (or polaronic shift) is 7700 cm$^{-1}$. Absorption lines of Cr$^{3+}$-Cr$^{2+}$ pair at
16720 cm$^{-1}$ and 19880 cm$^{-1}$ are associated with Cr$^{2+}$ ion excitation from the ground $^5E_g$ to excited $^3E'^a_g$ and $^3E'^b_g$ states. Energies of local vibrations in the ground and excited states of the pair are found to be 580±20 cm$^{-1}$, 540±20 cm$^{-1}$, 530±20 cm$^{-1}$, respectively.

Temperature dependence of integral intensities of absorption lines has been investigated. The evidence of Jahn-Teller effect in Cr$^{3+}$-Cr$^{2+}$ pair has been found; energy gap between Jahn-Teller minima of adiabatic potential of the pair center has been estimated as $\Delta_{JT} = 340 \pm 40$ cm$^{-1}$.

Important features of transitive region from double exchange to superexchange are pointed out. In particular it has been demonstrated that strong vibronic interaction in mixed valence pair center leads to crossover double exchange - ferromagnetic superexchange. Exchange integral for the ground state is $J = -14.9 \pm 0.4$ cm$^{-1}$.

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Figure captions

Fig.1. Absorption spectrum of KZnF$_3$:Cr$^{3+}$,Cr$^{2+}$ crystal at $T = 300$ K (a); derivatives of absorption spectra at $T = 300$ K (b) and $T = 150$ K (c).

Fig.2. Absorption spectra of KZnF$_3$:Cr$^{3+}$,Cr$^{2+}$ crystals with chromium ions concentrations $n$(Cr$^{3+}$)$=1.8 \cdot 10^{18}$ cm$^{-3}$, $n$(Cr$^{2+}$)$=9.2 \cdot 10^{18}$ cm$^{-3}$ (a,1) and $n$(Cr$^{3+}$)$=1.3 \cdot 10^{20}$ cm$^{-3}$, $n$(Cr$^{2+}$)$=7.3 \cdot 10^{18}$ cm$^{-3}$ (b,1); $T = 300$ K. Curves a,2 and b,2 are results of subtraction of the wing of absorption band with $\nu_{max} > 50000$ cm$^{-1}$ (dashed line) and $d-d$ bands of Cr$^{3+}$ ions.

Fig.3. Adiabatic potential for Cr$^{3+}$-Cr$^{2+}$ pair center in KZnF$_3$ crystal; charge-transfer transition is shown by the arrow.

Fig.4. Temperature dependence of integral intensity of Cr$^{3+}$-Cr$^{2+}$ pair absorption line at 16720 cm$^{-1}$ and its fitting by the models of the ground state with (a) and without (b) taking into account Jahn-Teller interaction.
