

Double exchange between chromium ions in a $\text{KZnF}_3:\text{Cr}^{3+},\text{Cr}^{2+}$ crystal

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Lines of absorption due to $\text{Cr}^{2+}-\text{Cr}^{3+}$ ion pairs have been observed in the optical spectrum of a KZnF_3 crystal activated with chromium ions. The absorption is accompanied by the dynamic transfer of an electron from one chromium ion to the other through an intermediate fluorine ion (a double 180° exchange). For the first time, the jump integral for an e_g electron has been determined directly from the temperature dependence of the integrated intensities of the lines: $|t_{uu}| = 1010 \pm 50 \text{ cm}^{-1}$. © 1995 American Institute of Physics.

1. The term “double exchange” was originally introduced by Zener¹ in an effort to explain the coexistence of conductivity and ferromagnetism in $(\text{La}_{1-x}\text{Ca}_x)(\text{Mn}_{1-x}^{3+}\text{Mn}_x^{4+})\text{O}_3$ compounds. A net positive charge (a hole) migrating through the sublattice of Mn^{3+} ions supports a conductivity. At the same time, it polarizes all the spins of the Mn^{3+} ions in one direction, since the direction of the spin of the hole does not change upon jumps between lattice sites. In other words, the conductivity is best in the case of a parallel orientation of the Mn^{3+} spins. Anderson and Hasegawa² examined an isolated pair of ions with one “extra” electron and showed that the spin-dependent part of the energy in the pair could not be described in terms of a product of spin operators of the type $(S_a S_b)$. The energy spectrum of a pair bound by double exchange does not obey the Landé interval rule; it is instead equidistant.

Despite the importance of double exchange (see a review³), there have been exceedingly few experimental studies of this topic, because serious difficulties confront such studies. The phase diagrams of mixed-valence materials are usually very complex. Attempts to extract the double-exchange parameter from macroscopic characteristics, in particular, the magnetization, have not been successful in practice. In the present letter we show that a great deal of progress can be made here by using a spectroscopic method involving crystals with a low concentration of pairs bound by double exchange. In this case the conductivity of the samples is still small, and it does not interfere with the penetration of light into the crystal.

2. The KZnF_3 crystals have the perovskite structure with space group $Pm3m$. Test samples were grown by the Bridgman–Stockbarger method using the fluorides of divalent and trivalent chromium. The concentration of the activators was varied from 0.1 to 1% by weight.

The absorption spectra of the test samples prepared in this manner exhibit the characteristic lines of Cr^{3+} and Cr^{2+} ions (Fig. 1). The wide bands shown in this figure,

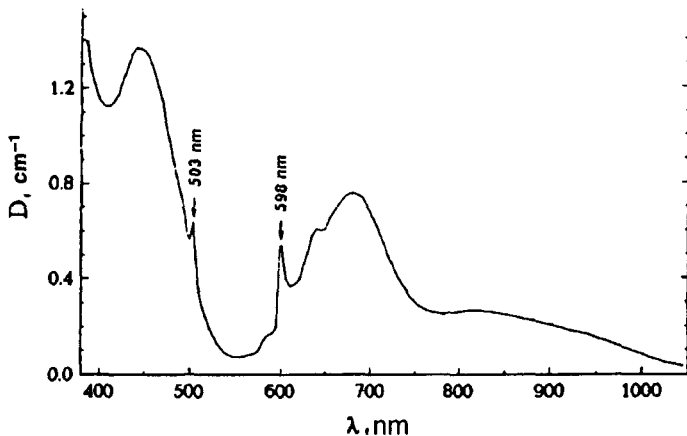


FIG. 1. Absorption spectrum of a $\text{KZnF}_3:\text{Cr}^{3+}, \text{Cr}^{2+}$ crystal at $T=300$ K.

peaking at 454 and 675 nm, stem from absorption of individual Cr^{3+} ions and are assigned to ${}^4A_{2g}-{}^4T_{1g}$ and ${}^4A_{2g}-{}^4T_{2g}$ transitions, respectively. The structure of the ${}^4A_{2g}-{}^4T_{2g}$ absorption band, seen in the form of dips, is due to manifestations of ${}^2T_{1g}$ and 2E_g states by virtue of a Fano antiresonance. The presence of Cr^{2+} ions in the crystals gives rise to a band with $\lambda_{\text{max}}=750$ nm in the spectrum, which corresponds to the ${}^5E_g-{}^5T_{2g}$ transition.

We also see in Fig. 1 that there are two groups of narrow lines in the spectrum, near 503 and 598 nm. They cannot be attributed to transitions of Cr^{2+} ions to states with a multiplicity of 3 or 1. The peak intensities of the lines at 503 and 598 nm are comparable to the absorption intensity in the wide bands of the Cr^{3+} and Cr^{2+} ions. The narrow lines in the absorption and luminescence spectra of iron-group ions at room temperature are due to transitions between states with identical configurations. These lines usually have a low intensity, since they are forbidden by a spin selection rule.

To learn about the nature of these lines in the absorption spectrum, we studied their intensity as a function of the concentrations of Cr^{3+} and Cr^{2+} ions in a fairly large number of samples. The concentrations of Cr^{3+} and Cr^{2+} ions were found from the intensities of the ${}^4A_{2g}-{}^4T_{2g}$ and ${}^5E_g-{}^5T_{2g}$ absorption bands, respectively. Since these bands overlap in the spectrum, we used the following procedure to determine their intensities: The shape of the ${}^4A_{2g}-{}^4T_{2g}$ absorption line was found from the spectrum of a crystal activated with Cr^{3+} ions exclusively. This spectrum was then multiplied by a certain factor and subtracted from the total spectrum in order to single out the absorption line of the Cr^{2+} ions.

It was found by this procedure that the intensity of the lines of unknown nature is proportional to the product of the concentrations of Cr^{3+} and Cr^{2+} ions. In particular, Fig. 2 shows the intensity of the absorption line with $\lambda=503$ nm as a function of this product of concentrations. Because of this circumstance, we can unambiguously interpret the narrow absorption lines as lines of binary centers of Cr^{3+} and Cr^{2+} ions. In this case we also see the reason for the anomalously large values of the oscillator strengths, since electric-dipole transitions become allowed for ion pairs by virtue of an exchange.⁴

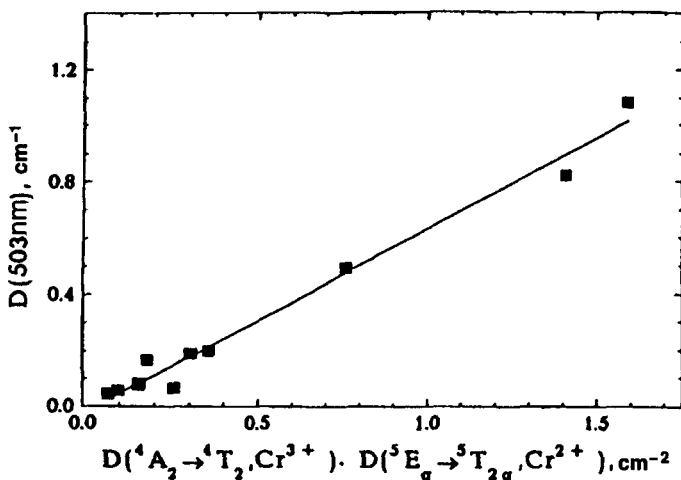


FIG. 2. Absorption intensity at the $\lambda = 503$ nm line versus the product of the concentrations of Cr^{3+} and Cr^{2+} ions. The latter concentrations were determined from the optical densities of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^5E_g \rightarrow {}^5T_{2g}$ absorption bands, respectively.

The states of pairs of ions with different charges are doubly degenerate with respect to interchange of the ions. The ions are coupled to the resultant spin of the pair, S_i , through the exchange of an electron from one ion to the other. In second quantization, the operator representing the jump of the "extra" electron is

$$\sum t_{\alpha\beta}(a_{\alpha}^{\dagger}b_{\beta} + b_{\beta}^{\dagger}a_{\alpha}), \quad (1)$$

where α and β specify the initial and final states of the migrating electron through the bridge fluorine ion. The ground states of the octahedrally coordinated $\text{Cr}^{3+}[t_{2g}^3({}^4A_{2g})]$ and $\text{Cr}^{2+}[t_{2g}^3({}^4A_{2g}), e_g; {}^5E]$ ions evidently exchange an e_g electron. One of the jump integrals, t_{uu} (involving σ bonds with an intermediate fluorine ion), is predominant. Using the Racah technique for cubic point groups,⁵ we can easily analyze the role played by the binding of the "extra" electron with the $t_{2g}^3({}^4A_{2g})$ ion core. The allowed values of the energy of the $\text{Cr}^{2+}-\text{Cr}^{3+}$ ion pair in the ground state are

$$E(S_0, S_i) = \pm |t_{uu}| \frac{(S_i + 1/2)}{4(2S_0 + 1)}. \quad (2)$$

The total spin of the pair, S_i , takes on the values $7/2$, $5/2$, $3/2$, and $1/2$. Here S_0 represents the spin of the core, which is $3/2$ in the case at hand.

The excited state of the $\text{Cr}^{2+}-\text{Cr}^{3+}$ ion pair, corresponding to the absorption line $\lambda = 503$ nm, corresponds to the ion states $\text{Cr}^{3+}[t_{2g}^3({}^4A_{2g})]$ and $\text{Cr}^{2+}[t_{2g}^3({}^4A_{2g}), e_g; {}^3E]$. As in the ground state of the pair, the migration of the e_g electron occurs along σ bonds. Now, however, the direction of the spin of the migrating electron is opposite the spin direction of the $t_{2g}^3({}^4A_{2g})$ core. The allowed values of the total spin of the pair, S_i^* , are now $5/2$, $3/2$, and $1/2$. A straightforward calculation shows that in this case the energy spectrum is given by an expression like (2):

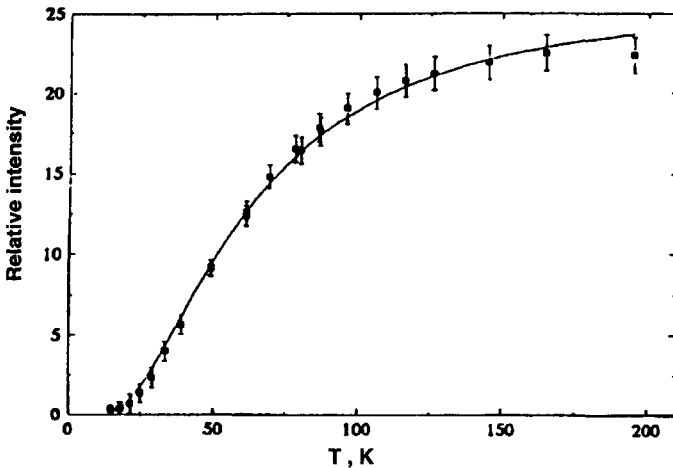


FIG. 3. Temperature dependence of the integrated intensity of the absorption line at $\lambda = 503$ nm, corresponding to the $\text{Cr}^{3+}-\text{Cr}^{2+}$ binary center.

$$E_{\text{ex}}(S_0, S_t^*) = \pm |t_{uu}^*| \frac{(S_t^* + 1/2)}{4(2S_0 + 1)}. \quad (3)$$

In other words, the spectrum is equidistant, as in the ground state. Within a small possible deviation of t_{uu} from t_{uu}^* , the scale of this equidistant spacing is the same. This result explains the observation of an isolated line at 503 nm which has no structure even at low temperatures.

To analyze the temperature dependence of the intensity of the absorption line at 503 nm, we note that there is no total-spin state $S_t = 7/2$ in the excited state of the pair. Electric-dipole transitions have a selection rule $\Delta S_t = 0$, so the line at 503 nm must be assigned to the $S_t(5/2) \rightarrow S_t^*(5/2)$ transition, and its temperature dependence should be described by a Boltzmann distribution. Figure 3 shows the measured dependence. It can indeed be approximated well by a Boltzmann distribution. We can thus determine the size of the energy gap, $E(S_t = 7/2) - E(S_t = 5/2)$, and therefore the value $|t_{uu}| = 1010 \pm 50 \text{ cm}^{-1}$.

We will not go into a detailed discussion of how we identify the other excited states of the pair. We simply note that the temperature dependence of the 598-nm line is similar and can be explained in precisely the same way.

3. In summary, this study has demonstrated (for the first time, to the best of our knowledge) that it is possible to measure the jump integral for the jump of an e_g electron between chromium ions in $\text{KZnF}_3:\text{Cr}^{3+}, \text{Cr}^{2+}$ quite reliably. It is obvious that measurements of this sort could be carried out for several other crystals, in particular, oxides. Our result here is of fundamental importance, having implications which go beyond the scope of this letter. The integral for the jumps between cations plays a fundamental role in modern theories of strongly correlated systems, in particular, in the famous t - J model. Reliable spectroscopic information on the parameter t is of fundamental importance.

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