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Low-symmetry effects in optical absorption of doped Tutton-salt crystals

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It is observed that the optical-absorption spectrum of Co^{2+} ions doped in low-symmetry Tutton-salt hydrated crystal hosts, recorded at room temperature, shows a large number of well-discernable bands only for the propagation of light along the optic axis. The good fit between the observed and calculated band positions strongly supports attributing the multifold structure in the spectrum to low-symmetry effects. Exchange-coupled Co^{2+}-Co^{2+} pairs have also been found to be formed in these crystals through the observation of combination bands attributed to simultaneous electron jumps in the neighboring cobalt ions.

I. INTRODUCTION

Tutton salts are a group of isomorphous compounds with the general chemical formula $M''M'_2(XO_4)_2 \cdot 6H_2O$, where M' is a monovalent cation, M'' is a divalent cation, and X is S or Se. The EPR studies[1-7] of Mn^{2+} ions doped in single crystals of such compounds show that the dopant ion substitutes for the host divalent cation. The EPR spectra also reflect the distortion of the water octahedron which surrounds the impurity ion.

The x-ray studies undertaken by Margulis and Templeton[8] in a typical Tutton-salt single crystal, magnesium ammonium sulfate hexahydrate (MASH), however, suggest that the water octahedron surrounding the divalent Mg^{2+} ion is not regular, but is slightly compressed along the body diagonal. As shown in Fig. 1, the polar bonds are slightly smaller than the axial bonds. Thus the crystalline field acting on the divalent ion is not cubic, and low-symmetry effects are expected. But no optical-absorption work so far seems to show such effects.

Daryan *et al.*[9] have reported optical absorption of Co^{2+} ions in isomorphous zinc ammonium sulfate hexahydrate (ZASH) Tutton-salt single crystals, but have not attempted the analysis of the spectra. Lakshmana Rao and Purandar[10] did, however, report an analysis of the absorption spectra of Co^{2+} ions doped in isomorphous zinc cesium sulfate hexahydrate (ZCSH) Tutton-salt single crystals. Further, the analysis of absorption spectra of Ni^{2+}-doped ZASH single crystals has been reported by Lakshman and Janardhanan.[11] Both the analyzed spectra consist of only a few absorption bands and could easily be fitted to a Hamiltonian representing the cubic crystalline field acting on the doped ion, due to the effect of the surrounding water octahedron.

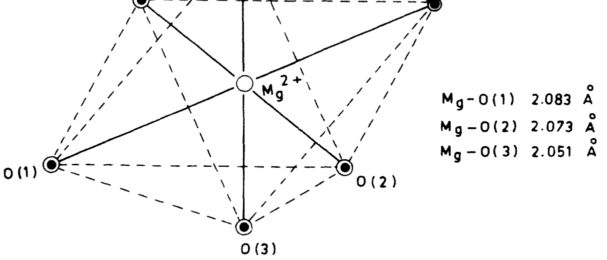

FIG. 1. Distortion of water octahedron in MASH.

In our recent work[12] we have reported that in the case of low-symmetry crystal hosts the spectrum, recorded for propagation of light in a random direction, loses its discernability due to sharp increase in the linewidth of bands by light-induced crystal-field fluctuations. It has further been verified experimentally that a true spectrum devoid of such undesired effects will result only when the light moves along the optic axis. It is to be noted that for some biaxial crystals the direction of the optic axis varies appreciably with the wavelength.[13,14] In such cases the optic axis alignment must be made for every wavelength. The phenomena as above has, however, escaped the attention of earlier workers, and analysis of spectra obtained for propagation of light perpendicular to a larger flat face has been presented.

In this work we are reporting absorption spectra for Co^{2+} ions doped in MASH and ZASH Tutton-salt single crystals in the optic-axis orientation, and a corresponding analysis, leading to the understanding of low-symmetry effects, even in the room-temperature (RT) spectra, is also presented.

II. EXPERIMENTAL

The crystals of MASH and ZASH were grown by slow evaporation of saturated acqueous solutions containing magnesium sulphate/zinc sulphate and ammonium sulphate in their equimolar ratio. The doping of Co^{2+} ions was made effective with the simultaneous addition of about 5 mol % of $CoSO_4 \cdot 7H_2O$. The crystals grew with known morphology and were pink in color. The spectra were recored at RT in the wavelength range of 3600–7000 Å with a Cary-17D spectrophotometer. For optic-axis orientation recordings, the crystal was simply mounted such that its optic axis for yellow Na light (almost center wavelength in the visible range) lay parallel to the incident beam. The resulting spectrum showed reasonably good discernability of bands, indicating that the dispersion of the optic axis is not appreciable in the present crystal system.

III. THE OBSERVED SPECTRA

Figure 2 gives the RT optical-absorption spectrum of Co^{2+} ions doped in MASH for propagation of light along an optic axis. This exhibits a good number of well discernable bands. However, when the spectrum was recorded perpendicular to the (110) plane, which is the larger flat face in grown samples, the multiple number of bands disappeared and the spectrum obtained (Fig. 3) was close to that reported by Daryan *et al.*[9] for Co^{2+}-doped ZASH and further similar to that reported by Lakshmana Rao and Purandar[10] for Co^{2+}-doped ZCSH, showing the importance of optic-axis orientation.

The spectra recorded for the ZASH host in this work were almost identical to those obtained for MASH and are thus not given separately.

IV. POSSIBLE ROLE OF LOW-SYMMETRY SPLITTINGS

The large number of bands (*A*, *B*, *C*, *D*, *E*, *F*, *G*, *H*, and *I*) obtained in the absorption spectra of Co^{2+}-doped Tutton-salt crystals in an optic-axis orientation cannot be attributed solely to the cubic-field splitting, and are possibly due to the effect of the low-symmetry crystalline field. Such low-symmetry field components are naturally expected in Tutton-salt single crystal hosts, because water octahedra are slightly distorted in MASH and would be so in isomorphous ZASH as well. The symmetry of the substituting Co^{2+} ions can thus be approximated to D_{4h} instead of the normally expected O_h symmetry. Such an approximation is necessary for direct comparison of our results with those for Co^{2+} ions in other hosts. In D_{4h} symmetry the different cubic-field energy levels of Co^{2+} ions would split and their orbital degeneracies would be reduced, as shown in Fig. 4. The different excited states with symmetries A_{1g}, A_{2g}, T_{1g}, and T_{2g} would get modified and/or split in the field of D_{4h} symmetry as follows:

$$A_{1g} \rightarrow A_{1g} ,$$

$$A_{2g} \rightarrow B_{1g} ,$$

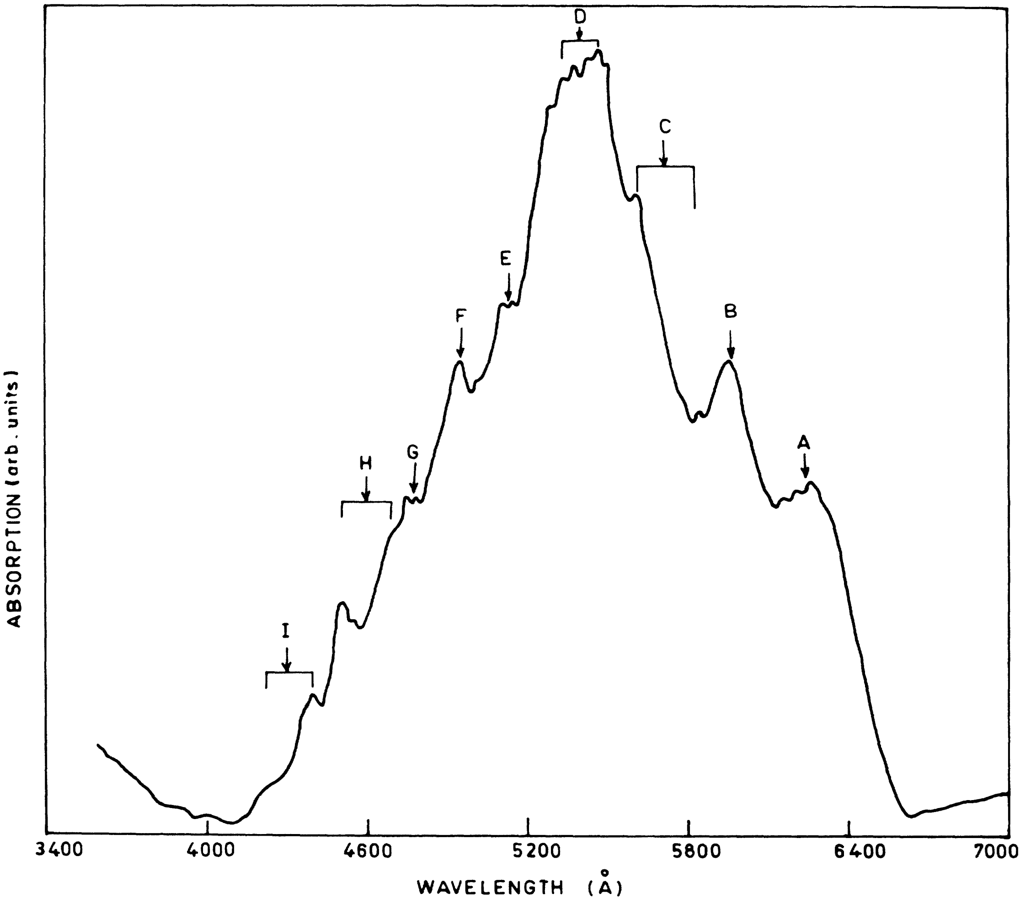

FIG. 2. Optical-absorption spectrum of Co^{2+}-doped MASH for propagation of light (unpolarized) along an optic axis.

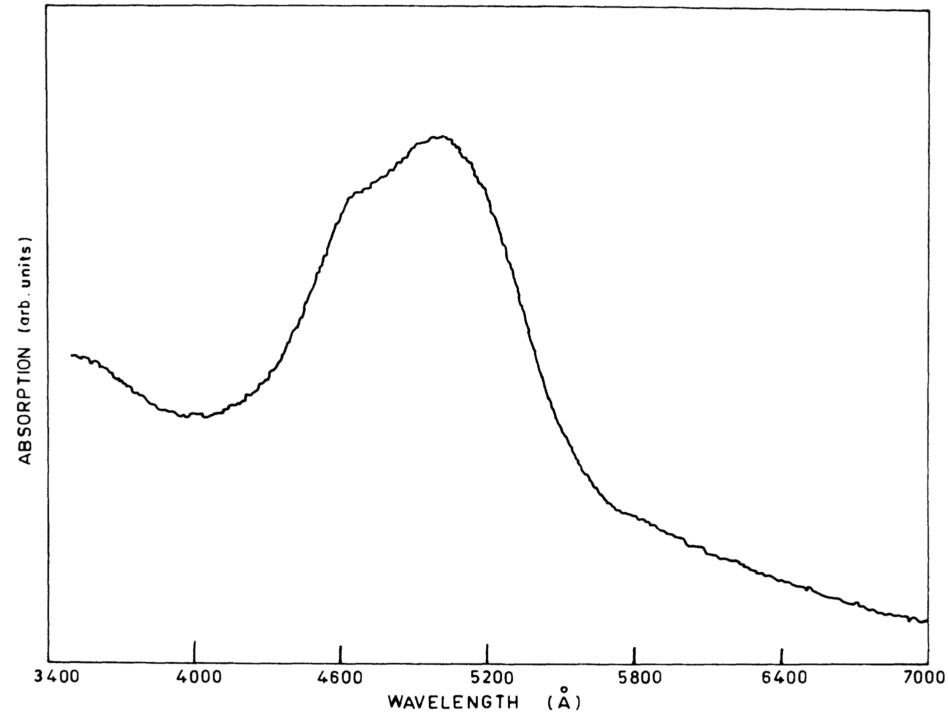

FIG. 3. Optical-absorption spectrum of Co^{2+}-doped MASH for propagation of light (unpolarized) perpendicular to the crystal (110) plane.

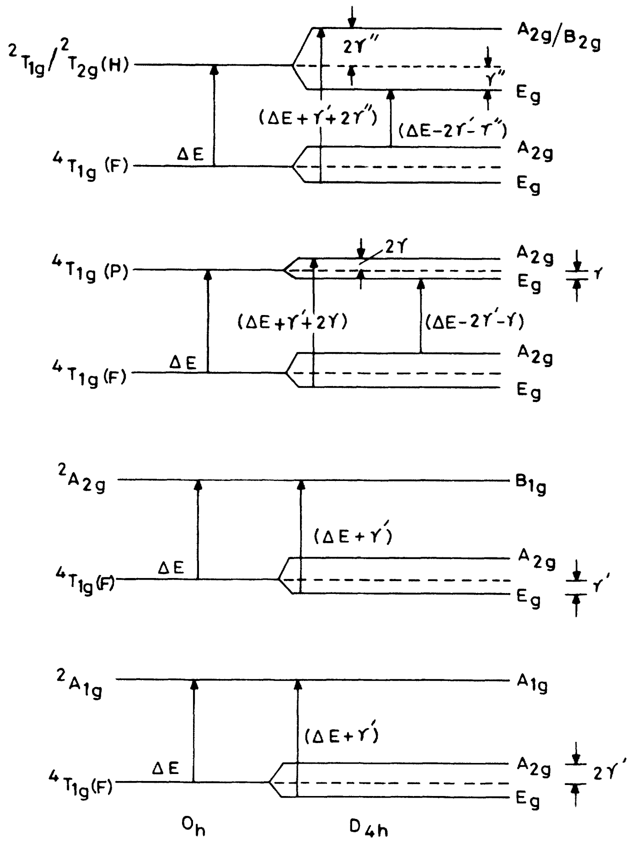

FIG. 4. Splittings and/or modifications of octahedral field energy levels under tetragonal distortion.

$$T_{1g} \to A_{2g} + E_g ,$$

$$T_{2g} \to B_{2g} + E_g ,$$

For the $^4T_{1g}(F) \to {}^4T_{1g}(P)$ cubic-field transition one may thus expect four transitions between two pairs A_{2g} and E_g. However, only two transitions,

$$^4A_{2g}(T_{1g}(F)) \to {}^4E_g(T_{1g}(P))$$

and

$$^4E_g(T_{1g}(F)) \to {}^4A_{2g}(T_{1g}(P)) ,$$

are allowed as per group-theoretical considerations. It may be realized here that with kT equaling about 200 cm^{-1} at RT, the $^4A_{2g}$ level would be sufficiently populated along with the lowest ^4E_g level.

The details of splittings (not to scale) for different transitions are evident from Fig. 4. In this figure, different energy differences ΔE represent the separations of energy levels of various transitions in octahedral symmetry. The first-order corrections to the low-symmetry field have been incorporated in terms of parameters r, r', and r'', with $3r$ representing the total splitting of the T_{1g} level originating from the ^4P level, $3r'$ the splitting of the T_{1g} level originating from the ^4F level, and $3r''$ the splitting of the $^2T_{1g}$ and/or $^2T_{2g}$ levels originating from the ^2H levels. As in Fig. 4 it may further be realized that the energy separations of transitions $T_{1g} \to A_{1g}$ and $T_{1g} \to A_{2g}$ would simply be increased by r' due to low-symmetry splittings.

It is obvious that low-symmetry crystal-field splittings as above leading to pairs of split bands would not arise for an ion having a nondegenerate ground state in the cubic field. In such a situation only a small shift of band positions would occur. For example, in the case of Ni^{2+} ions doped in MASH (Ref. 15) and thus having D_{4h} site symmetry, the ${}^3T_{1g}$ excited state of the transition ${}^3A_{2g} \rightarrow {}^3T_{1g}$ would split into two states with symmetry A_{2g} and E_g, and only one transition ${}^3A_g \rightarrow {}^3E_g$ would be finally allowed to cause a small shift ($\approx r'$ cm^{-1}) of band positions. This fact can elude the attention of workers, as a fitting of band positions can always be made to some extent, and may be the reason why Ghosh and Mukerjee[16] did not report low-symmetry splittings in the spectrum of Ni^{2+}-doped Cs_2CdCl_4 along the optic axis.

V. BAND POSITIONS IN THE CUBIC-FIELD APPROXIMATION

Four pairs of band C, D, H, and I have been observed at (16 995, 17 680 cm^{-1}), (18 140, 18 485 cm^{-1}), (21 050, 21 910 cm^{-1}), and (22 500, 23 320 cm^{-1}) with separations 685, 345, 860, and 820 cm^{-1}, respectively. The pairs H and I could be easily located. However, to locate the positions of pairs C and D, help was also taken from slightly off the optic-axis spectrum, where the fine structure was eliminated. These four pairs have been assigned as the low-symmetry field components of transitions ${}^4T_{1g}(F) \rightarrow {}^2T_{1g}(H)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^4T_{1g}(F) \rightarrow {}^2T_{2g}(H)$, and ${}^4T_{1g}(F) \rightarrow {}^2T_{1g}(H)$. Thus the second pair is expected to have a separation $3(r+r')$ and others a separation of $3(r'+r'')$ each.

The individual values of r, r', and r'' cannot be obtained by simply knowing the numerical values of the two terms $(r+r')$ and $(r'+r'')$. However, the splittings of different triplet levels originating from parent P, F, and H states are expected to depend upon corresponding orbital quantum numbers. One may thus presume r, r', and r'' to have values in the ratio 1:3:5. Using this ratio, the values of the r parameter can be obtained independently from any of the four doublet separations as above. The different values obtained are, however, close to 32 cm^{-1} within 10% tolerance. This supports the validity of our assumption about the relative values of the r parameters.

Now taking r' ($\equiv 3r$) to be 96 cm^{-1}, the positions of the ${}^4T_{1g}(F) \rightarrow {}^2A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^2A_{1g}(G)$ transitions in the absence of low-symmetry effects could accordingly be estimated to be 16 644 and 19 874 cm^{-1}, respectively. Further in the first order of perturbation, the estimated position of the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition can be obtained by adding r to the average of the observed positions of two bands in the second pair. The estimated positions of ${}^4T_{1g}(F) \rightarrow {}^2T_{1g}(H)$, ${}^4T_{1g}(F) \rightarrow {}^2T_{2g}(H)$, and again ${}^4T_{1g}(F) \rightarrow {}^2T_{1g}(H)$ are, however, obtained by subtracting r from the average of corresponding observed pairs of bands. The averaging process is clearly indicated in Table I. The various transition energies as corrected above for low-symmetry effects were subsequently fitted to the energy matrices for cubic field symmetry, given by Tanabe Sugano,[17] and a best fit for the values of B, C, and D_q was done on a DEC-10 computer. The different relevant parameters thus obtained are

$$B = 776\ cm^{-1},$$

$$C = 2999\ cm^{-1},$$

$$D_q = 884\ cm^{-1},$$

$$r = r'/3 = r''/5 = 32\ cm^{-1}.$$

The calculated band positions using the above set of parameters are further given in Table I, and it is seen that a good match exists between the observed and estimated band positions, thus justifying our presumption about attributing the structure in the spectrum to low-symmetry effects. The small mismatch could be attributed to two facts. First, there may exist some dispersion in the optic axis. Secondly, the estimation of experimental band positions in the cubic field approximation was approximate, done for simplicity, by taking simply the average of low-symmetry split-band positions.

So far a strong band at 15 920 cm^{-1} (marked A) and two weak bands at 19 370 (marked E) and 20 765 cm^{-1} (marked G) have been left unassigned. However, the band of 15 920 cm^{-1} occurs at approximately twice the calculated value of 7780 cm^{-1} for the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$. The band of 19 370 cm^{-1} may be interpreted as a combination of the 5726-cm^{-1} ${}^4T_{1g}(F) \rightarrow {}^2E_g(G)$ band with the 13 383-cm^{-1} ${}^4T_{1g}(F) \rightarrow {}^2T_{2g}(G)$ band and further the band of 20 765 cm^{-1} may be interpreted as a combination of the 7780-cm^{-1} band with the 13 057-cm^{-1} ${}^4T_{1g}(F) \rightarrow {}^2T_{1g}(G)$ band. The observation of such combination bands is quite likely in the present system, as exchange-coupled Co^{2+}-Co^{2+} pairs are expected to exist in appreciable number due to the large content (5% by weight) of cobalt in the crystals. In Co^{2+}-Co^{2+} pairs, the two ions could probably simultaneously be excited by a photon of incident light giving appreciable intensity to the observed band.

It would, however, be interesting to undertake measurements of spectra in samples with different Co^{2+} concentrations. In low-concentration samples the intensity of the Co^{2+}-Co^{2+} pair bands must decrease in relation to those of single Co^{2+} ions and accordingly the assignment of combination bands could be confirmed.

VI. SPIN-ORBIT EFFECTS

Lakshmana Rao and Purandar[10] had assumed preponderance of spin-orbit effects over the crystal-field effects for Co^{2+}-doped ZCSH. They took the spin-orbit parameter to be as large as 500 cm^{-1}, but were not successful in explaining the observed spectra. Their results thus do not yield strong support for the existence of large spin-orbit coupling in a Co^{2+}-doped system. Koidl,[18] however, has observed well-resolved spin-orbit splittings at 4.2 K in the optical-absorption spectra of Co^{2+}-doped ZnO and explained the separations of 5.4 and 18.9 cm^{-1} in the two pairs of spin-orbit components in the ${}^4T_2$ band with a spin-orbit parameter of 431 cm^{-1}. As is clear from Fig. 2 in the present study, as well, a semiresolved structure with splittings of the order of 20 cm^{-1} is seen in almost all the strong bands of optical-absorption spectra recorded with the propagation of light along an optic

TABLE I. The observed, estimated (for cubic field) and calculated (both for cubic and low-symmetry fields) band positions in the optical absorption of cobalt ions doped in MASH.

Observed band positions (cm^{-1})	Estimated positions neglecting low-symmetry field (cm^{-1})	Calculated positions (cm^{-1})		Identification in figure	Assignment
		In cubic field	In low-symmetry field		
		5726			${}^4T_{1g}(F)\rightarrow{}^2E_g(G)$
		7780			${}^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$
		13 057			${}^4T_{1g}(F)\rightarrow{}^2T_{1g}(G)$
		13 383			${}^4T_{1g}(F)\rightarrow{}^2T_{2g}(G)$
15 920		15 560		*A*	2×7780
16 740	16 644	16 620	16 716	*B*	${}^4E_g(T_{1g}(F))\rightarrow{}^2B_{1g}(A_{2g}(F))$
16 995	17 306	17 272	16 920	*C*	${}^4A_{2g}(T_{1g}(F))\rightarrow{}^2E_g(T_{1g}(H))$
17 680			17 688		${}^4E_g(T_{1g}(F))\rightarrow{}^2A_{2g}(T_{1g}(H))$
18 140	18 345	18 361	18 137	*D*	${}^4A_{2g}(T_{1g}(F))\rightarrow{}^4E_g(T_{1g}(P))$
18 485			18 521		${}^4E_g(T_{1g}(F))\rightarrow{}^4A_{2g}(T_{1g}(P))$
19 370		19 109		*E*	5726+133 383
19 970	19 874	19 881	19 977	*F*	${}^4E_g(T_{1g}(F))\rightarrow{}^2A_{1g}(A_{1g}(G))$
20 765		20 837		*G*	7780+13 057
21 050	21 448	21 486	21 134	*H*	${}^4A_{2g}(T_{1g}(F))\rightarrow{}^2E_g(T_{2g}(H))$
21 910			21 902		${}^4E_g(T_{1g}(F))\rightarrow{}^2A_{2g}(T_{2g}(H))$
22 500	22 878	22 844	22 492	*I*	${}^4A_{2g}(T_{1g}(F))\rightarrow{}^2E_g(T_{1g}(H))$
23 320			23 260		${}^4E_g(T_{1g}(F))\rightarrow{}^2A_{2g}(T_{1g}(H))$

axis. Thus moderate spin-orbit effects could exist in the present system. No attempt has been made presently to calculate the spin-orbit parameter involved, because of the multiplicity of structure in the bands. The low-temperature measurements could, however, prove useful in this direction, leading to better resolution of spin-orbit components along with improved discernability of spectra with regard to low-symmetry bands.

VII. CONCLUSION

It is understood that if the spectra are not recorded for optic-axis orientation, even the best possible efforts, such as those made by different workers in the past, towards analyzing the observed spectra may end up in vain. The proper mode of recording helps to view even the low-symmetry crystal-field effects, through optical-absorption studies made at RT itself. This work thus brings the optical studies at par with x-ray investigations. The observation of two electron jumps in exchange-coupled Co^{2+}-Co^{2+} pairs is another achievement, which would attract the attention of the scientific community interested in magnetic materials to invoke greater use of optical tools for such studies.

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