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Optical spectra of manganous ion in magnetic trimethyl ammonium manganous trichloride dihydrate $[(CH_3)_3NH]MnCl_3 \cdot 2H_2O$ single crystals

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The low-temperature polarized absorption spectra of the Mn^{2+} ion in the orthorhombic $[(CH_3)_3NH]MnCl_3 \cdot 2H_2O$ single crystal have been reported at different temperatures. The spectra reveal C_i site symmetry for the transition center. Metal-pair interaction is invoked to rationalize the polarization characteristics of absorption bands. This interaction produces some remnants of C_{2h} selection rules. The absorption bands are observed either as magnon sidebands or magnon-phonon sidebands. The influence of the molecular field at the lowest temperature is proposed to be responsible for splitting some of the absorption lines.

I. INTRODUCTION

The effects of magnetic ordering on the electronic spectra of a collection of transition-metal ions have been a subject of considerable interest to spectroscopists and solid-state physicists. Such studies concentrate on linear-chain ferro- and antiferromagnets that involve detailed investigations of sideband structure. The polarization characteristics of the sideband, as well as their magnetic-field dependence, help to understand the cooperative exchange phenomenon and lead to the establishment of the presence of internal molecular field and determine the spin-flop transition.[1-6] Because of their spin-forbidden nature, several of the absorption bands for Mn^{2+} ions in crystals have considerably narrow bandwidths. Since the magnitude of interactions are small due to exchange-related processes, the possibility of their detection improves with the sharpness of the absorption bands and is most likely to show up in spin-forbidden transitions that have narrow bandwidths.[7] Hence the optical study of the magnetic trimethyl ammonium manganous trichloride dihydrate $[(CH_3)_3NH]MnCl_3 \cdot 2H_2O$ (hereafter will be called TrMAMC crystal) single crystal might be useful in this context.

The reported magnetic susceptibility[8,9] for this magnetic crystal has shown them to be antiferromagnetically ordered at the lowest temperature ($T_N \simeq 1$ K) with canted spin structure. In this paper we discuss the polarized absorption spectra of TrMAMC single crystal at different temperatures and at various orientations of the incident polarized light. The spectra data have been used to determine the symmetry of the transition site, to understand the mechanism of the transition, and to corroborate the appearance of any cooperative phenomenon in the optical transition. A survey of absorption spectra of this orthorhombic Mn^{2+} crystal have been reported up to 77 K.[10,11] In two such reports contrasting claims of negligible to large orthorhombic crystal-field (CF) splitting have been made. We offer evidences and assignments in support of orthorhombic splitting energies ranging from 50 to over 600 cm^{-1} within the quartet energy levels.

II. EXPERIMENTAL DETAILS

Single crystals of TrMAMC were prepared from aqueous solution using equimolar mixture of trimethylammine hydrochloride $(CH_3)_3NHCl$ and $MnCl_2 \cdot 4H_2O$. The crystals were light pink in color and grew as elongated prisms. The orthorhombic[12] crystals of TrMAMC belong to the space group Pnma with $a = 16.779$, $b = 7.434$, and $c = 8.227$ Å, $Z = 4$. Viewed under polarizing microscope the crystals show strong optical dichroism. Minimum dichroism is observed when the polarized light propagates along the a axis of the crystal. Thus the a axis of the crystal was identified while the elongated side was its b axis and the third axis was identified from the fact that the bc plane is a cleavage plane of the crystal. It is isostructural with its cobalt analogue. Thus crystals can be easily oriented along any direction quite correctly.

The manganese atoms lie on crystallographic centers of inversion symmetry and are octahedrally coordinated to four chlorine atoms and two oxygen atoms of the water molecules. The octahedra share edges to form an infinite chain running parallel to crystallographic b direction. The manganese atoms are 3.717 Å apart and are linked by bridging chlorine atoms. The polymeric chains are cross linked in the crystallographic c direction through hydrogen bonding.

The absorption spectra were recorded with a Cary 17D spectrophotometer. The incident light was polarized by means of a Glan Taylor prism placed in the sample compartment. The crystal was oriented under polarizing microscope, as mentioned earlier, and mounted over a pinhole in a small copper sheet which was bolted to the sample holder at the base of an Air Product closed-cycle helium-refrigerator Displex cryostat. The spectra were measured at several temperatures between 300 and 15 K with polarizing light passing along three principal crystallographic directions (a,b,c). High-resolution spectra were recorded photographically using a plane grating spectrograph (Zeiss PGS 2) which has a dispersion of about 3.5 Å/mm in the first order.

III. RESULTS AND DISCUSSION

The polarized absorption spectra, which have been recorded at different temperatures, are shown in Figs. 1–3 and relevant absorption results are given in Tables I–III. At room temperature there are four principal absorption regions around 18 500–19 800 cm^{-1} (region I), 21 000–23 900 cm^{-1} (region II), 23 800–24 700 cm^{-1} (region III), and 26 800–29 000 cm^{-1} (region IV). At 15 K, while the bands in regions I and II remain broad and have shown splitting only into two or three components, the bands of region III and IV become quite sharp and intense and they resolved into several fine structures.

The absorption bands have shown marked polarization features and the polarized spectra recorded with electric vector parallel to the crystallographic a axis $(\mathbf{E}\|\hat{\mathbf{a}})$ are quite different from the other two polarized spectra recorded with $\mathbf{E}\|\hat{\mathbf{b}}$ and $\mathbf{E}\|\hat{\mathbf{c}}$ which were more or less similar. The two $\mathbf{E}\|\hat{\mathbf{a}}$ spectra recorded with light propagating along crystallographic b and c directions are identical in nature. Hence the transitions are governed by electric dipole mechanism.[13] The integrated intensity of the absorption band shows about 10% increase with decrease in temperature from 100 to 15 K, which suggests that either exchange related mechanism or mixing of opposite parity states through odd CF terms in a noncentrosymmetric site contribute to the intensity. Since the intensity shows no enhancement on increase in temperature vibronic mechanism is excluded from consideration. The difference in polarized spectra for $\mathbf{E}\|\hat{\mathbf{a}}$ and $\mathbf{E}\|\hat{\mathbf{b}}$ indicates that the site symmetry is lower than D_{4h} and the actual symmetry of the transition site is orthorhombic. The initial assignment of the spectra were done by performing a crystal-field calculation in O_h symmetry and by comparison with Tanabe-Sugano diagrams. The four regions of absorption are attributed to transitions from ground $^6A_{1g}$ state to the cubic field components $^4T_{1g}(G)$ (region I), $^4T_{2g}(G)$ (region II), $^4A_{1g}$, $^4E_g(G)$ (region III), and $^4T_{2g}$, $^4E_g(D)$ (region IV), respectively. (Here we give the orbital angular momentum label for the principle Russel-Saunders term in parentheses.) Now an attempt is made to explain the polarization of the absorption bands assuming them to be due to transition from ground $^6A_{1g}$ to the excited orthorhombic CF states. In a noncentrosymmetric orthorhombic site (D_2 or C_2) the absorption bands of region I should consist of three bands, each of which is strongly polarized either in one or in two of the three crystallographic directions as they result from ground ^6A to excited orthorhombic CF split components

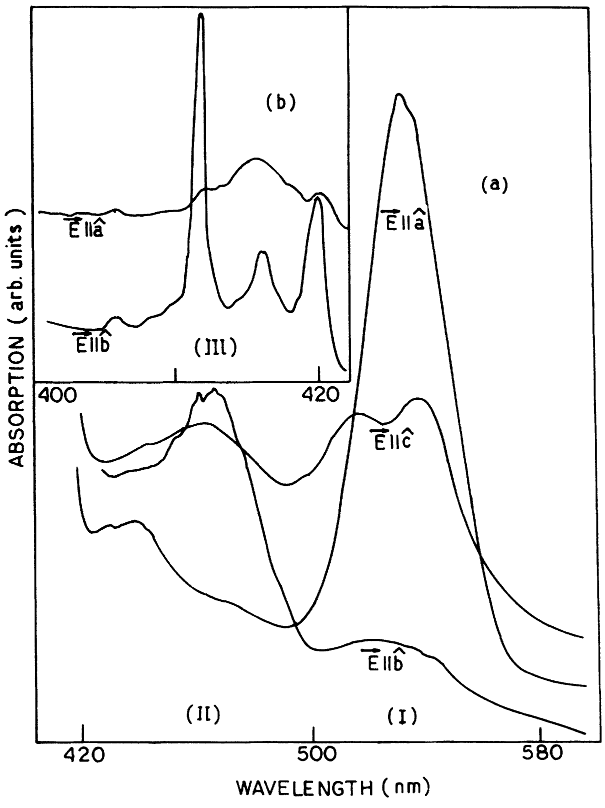

FIG. 1. (a) Polarized absorption spectra of $[(CH_3)_3NH]MnCl_3{\cdot}2H_2O$ crystal at 15 K of the regions I and II. (b) Polarized absorption spectra of $[(CH_3)_3NH]MnCl_3{\cdot}2H_2O$ crystal at 15 K for the region III.

TABLE I. Selection rules for spin-dependent exchange-induced electric dipole transitions.

Symmetry of excited states for various site symmetries			Polarization of light	
			Index of dipole operator	Allowed transitions
$D_{2h}(a)$	$C_{2h}(a)$	C_i	δ	$\mathbf{E}\|^{a}\ldots$
A_g	A_g	A_g	$y(x)$	$\hat{\mathbf{b}}(\hat{\mathbf{c}})$
B_{1g}	A_g	A_g	$x(y)$	$\hat{\mathbf{c}}(\hat{\mathbf{b}})$
B_{2g}	B_g	A_g	z	$\hat{\mathbf{a}}$
B_{3g}	B_g	A_g	(z)	$(\hat{\mathbf{a}})$

[a] Polarizations given in parentheses are forbidden for D_{2h} symmetry; all polarizations are allowed for C_i symmetry.

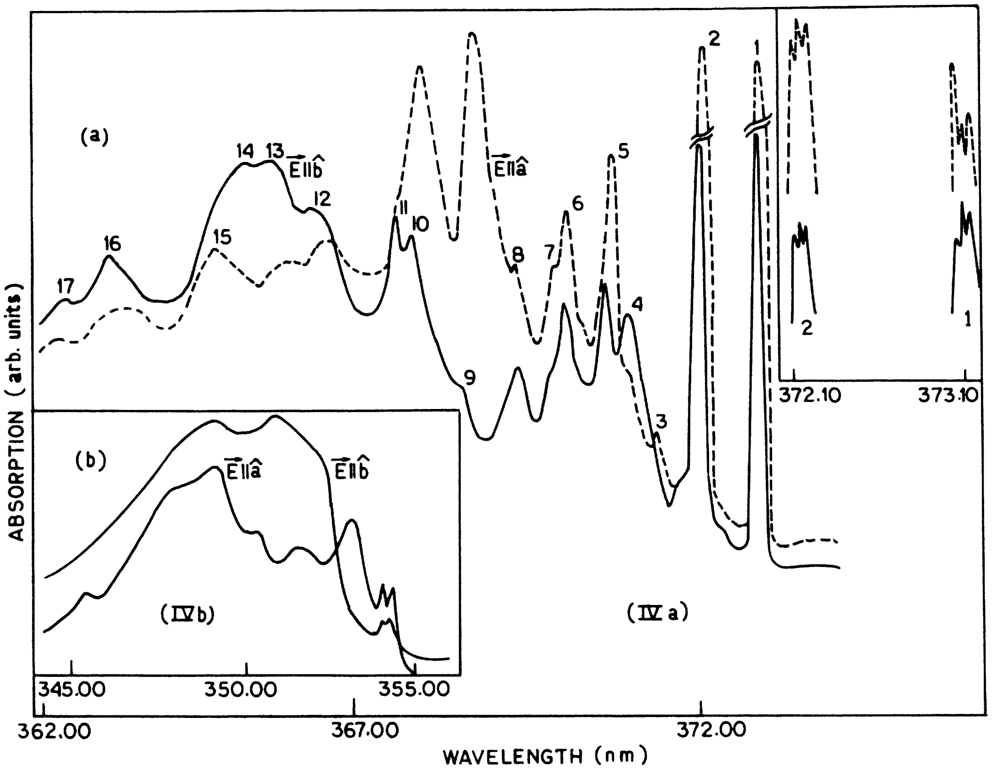

FIG. 2. (a) Polarized absorption spectra of $[(CH_3)_3NH]MnCl_3 \cdot 2H_2O$ at 15 K for the region IVa. Fine structures of lines 1 and 2 at the lowest temperatures are shown in the inset at the right-hand corner of the figure. (b) Polarized absorption spectra of $[(CH_3)_3NH]MnCl_3 \cdot 2H_2O$ crystal at 15 K for the region IVb.

of $^4T_{1g}$ cubic state. But no such polarization characteristics have been observed for the absorption bands of region I. Similarly the polarization characteristic of the absorption bands of the other regions too could not be rationalized within the selection rule for the noncentrosymmetric orthorhombic transition site. Hence it is inferred that the center of inversion of the transition site is maintained.

The other way to explain the electric dipole allowedness of the absorption bands is to invoke weak metal-pair interaction. The nonexponential temperature dependence of the absorption bands is indicative of spin-dependent transition mechanism, which involves interaction of an ion pair with the radiation field. The matrix elements of spin-dependent transition moment P_{jl} for an ion pair j and l corresponding to transition from ground state with $M_j = M$ to $M_l = -S$ to excited state μ and $M_l' = -S+1$ is expressed as[14,15]

$$\langle \mu M_l' | P_{jl}^{\delta} | M, M_l \rangle = \sum a_{\mu}^{*}(M'm)\pi_m^{\delta}(j*l)$$

$$\times \langle M' | \sigma_j | M \rangle \langle -S+1 | S_l | -S \rangle ,$$

where δ is the index of the dipole operator and can be associated with the polarization of the light. The definition of other quantities involved in the expression has been given by Fujiwara and Tanabe.[14] If we assume that

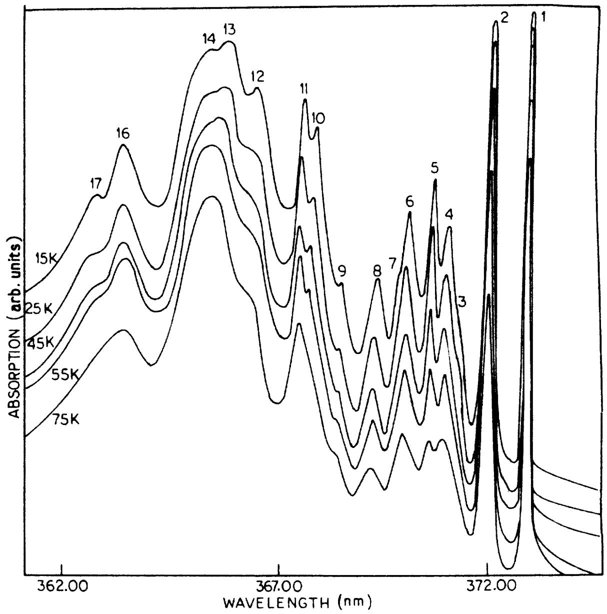

FIG. 3. Absorption spectra of Mn^{2+} in $[(CH_3)_3NH]MnCl_3 \cdot 2H_2O$ crystal for polarization E∥b̂ as a function of temperature for region IVa.

sufficient π_γ^δ are only significant for the nearest pairs along the b axis, then the polarization selection rule for orthorhombic D_{2h} (C_{2h}) symmetry can be easily calculated following Fujiwara and Tanabe.[14] The results are given in Table I. The principle selection rule for C_{2h} symmetry is that absorption for one polarization is different from that of the other two. To explain the unique dichroism of the TrMAMC crystals the a crystal axis should be C_2 symmetry axis. To determine whether this axis is a reasonable choice for local site symmetry we have analyzed the effect of C_2 operations on the four nearest-neighbor chlorines and two nearest-neighbor oxygens around a Mn atom. The quality of near symmetry for each rotation (i.e., twofold rotations around crystal a, b, and c axes, respectively, which are given in parenthesis) is summarized in terms of the displacement of a rotated atom from the starting location of the corresponding atom with which it should be symmetric. The displacement of the two oxygens and four chlorines, i.e., the six nearest-neighbor atoms from their initial position after twofold rotation are given in the following:

$C_2(c)$: 2 O, 0.948 Å; 2 Cl(1), 0.011 Å; 2 Cl(2), 1.060 Å
$C_2(b)$: 2 O, 0.565 Å; 4 Cl, 0.536 Å
$C_2(a)$: 2 O, 0.762 Å; 4 Cl, 0.524 Å.

TABLE II. Frequencies of absorption bands (cm^{-1}) of TrMAMC single crystal at 15 K.

	Frequency (cm^{-1})		Principal polarization of bands $\mathbf{E}\Vert\hat{\mathbf{a}}$, $\hat{\mathbf{b}}$, or $\hat{\mathbf{c}}$
I	18 520		a,c
	18 760		a
	19 230		c
II	21 500		b,c
	22 730		a,c
	23 200		a
III	23 810	I	b,c
	23 925	I+115	a
	24 025	I+215	a,b,c
	24 110		b
	24 280	II	b,c
	24 390	II+110	b
	24 485	II+205	b
	24 650	III	a,b
IV(a)	1. 26 810	I	a,b,c
	2. 26 870	II	a,b,c
	3. 26 935 (weak)	I+125	
	4. 26 955	I+145	b,c
	5. 26 970	II+100	a,b,c
	6. 27 015	I+205	a,b,c
	7. 27 035	I+225	c
	8. 27 070	II+200	b,c
	9. 27 120	III	a
	10. 27 180	IV	a
	11. 27 200	III+100,V	b,c
	12. 27 285	IV+100	a,b,c
	13. 27 340	III+220	b,c
	14. 27 385	IV+250	b,c
	15. 27 410	III+100+210	a
	16. 27 530	III+2×200	a,b,c
	17. 27 575	IV+2×205	a,b,c
IV(b)	28 215	I	a,b,c
	28 235	I′	a,b,c
	28 330	I+115	a
	28 430	I+215	a
	28 465	I′+2×115	b
	28 545	II	a
	28 645	II+100	a,b,c
	28 760	II+215	a
	28 975	II+2×215	a

TABLE III. Orthorhombic CF energy levels of Mn^{2+} in TrMAMC crystal showing descent in symmetry. Crystallographic axis for principal point-group axis is shown in parentheses.

O_h	$D_{4h}(c)$	$D_{2h}(a)$	$C_{2h}(a)$	Energy (cm^{-1})
$^6A_{1g}(S)$	$^6A_{1g}$	^6A_g	^6A_g	0
$^4T_{1g}(G)$	$^4A_{2g}$	$^4B_{3g}$	^4B_g	18 520
	^4E_g	$^4B_{2g}$	^4B_g	18 760
		$^4B_{1g}$	^4A_g	19 230
	^4E_g	$^4B_{1g}$	^4A_g	21 500
$^4T_{2g}(G)$		$^4B_{2g}$	^4B_g	22 730[a]
	$^4B_{2g}$	$^4B_{3g}$	^4B_g	23 200[a]
$^4A_{1g}(G)$	$^4A_{1g}$	^4A_g	^4A_g	23 810
$^4E_g(G)$	$^4A_{1g}$	^4A_g	^4A_g	24 280
	$^4B_{1g}$	^4A_g	^4A_g	24 650
	^4E_g	$^4B_{1g}$	^4A_g	26 840[b]
$^4T_{2g}(D)$		$^4B_{2g}$	^4B_g	27 150[b]
	$^4B_{2g}$	$^4B_{3g}$	^4B_g	27 200
$^4E_g(D)$	$^4A_{1g}$	^4A_g	^4A_g	28 215
	$^4B_{1g}$	^4A_g	^4A_g	28 545

[a] Energy values have large error bars because of broadness and diffuseness of the absorption band.

[b] Original levels have shown large spin-orbit splitting. The energy is only the average of two Kramer's doublets.

Comparison of these displacements with the distance of the corresponding atom from central Mn atom [i.e., 2 O, 2.18 Å; 2 Cl(1), 2.52 Å, and 2 Cl(2), 2.58 Å] provide very little indication for a higher symmetry than the actual C_i site symmetry. But the unique absorption characteristics of a axis polarization for the electric vector indicate there is some strong local distinction of this a axis. The most likely cause of this special significance of the a axis seems to be that the spins should be expected to lie in the bc plane.[8,9] Then $C_2(a)$ should be the principle symmetry axis. Hence in our case $z=a$, $y=b$, and $x=c$. The principle axes x,y,z of an orthorhombic field around the Mn^{2+} ion, where z is the C_{2h} symmetry axis, are determined by the fact that the ground-state spins of $\frac{5}{2}$ lie in the bc plane and that $C_2(a)$ is a better approximate symmetry for this complex than $C_2(c)$.

One can construct a descent in symmetry table to connect the representation of $D_{4h}(c)$, where the C_4 axis is the crystal c direction, with those of $D_{2h}(a)$ and $C_{2h}(a)$. These results are given in Table III. A comparison of the predicted polarization in Table I with the observed polarizations of the absorption bands clearly indicates that the site symmetry of the metal ion in the crystal is only C_i with some remnants of C_{2h} selection rules. The absorption bands seem to be all of cold magnon or magnon-phonon sideband type and the true origin is too weak to locate. Since the cold magnon sidebands appear on the high-energy side of the true origin, an estimate of magnon density of states may assist in locating the real position of the excited CF states. However, an analysis of the polarization of the absorption bands may lead to a reasonably good prediction of the excited state (even if they are magnon sidebands), since for broad bands the error of energy determination is large. Such an analysis of the four different absorption region is given in the following.

Since the $^4T_{1g}$ state will split into one ^4A_g and two ^4B_g states in orthorhombic C_{2h} site[16] and transition to ^4A_g state is polarized $\mathbf{E}\|\hat{\mathbf{b}},\hat{\mathbf{c}}$ and that to ^4B_g state is polarized $\mathbf{E}\|\hat{\mathbf{a}}$, the dominance of intensity in a polarization in the region I is in good agreement with theoretical expectation. In region II the dominance of intensity is in bc polarization, which agrees with the selection rule, as the transition to a ^4A_g orthorhombic state is polarized $\mathbf{E}\|\hat{\mathbf{b}},\hat{\mathbf{c}}$. The absorption bands in polarization $\mathbf{E}\|\hat{\mathbf{b}}$ have shown several fine structures but they are not sufficiently well resolved to enable us to analyze them. In region III, a phonon progression of 110 and 210 cm^{-1} based on two of the three origins have been observed. In region IV the absorption spectra have been grouped together into two parts spanning 26 800–27 600 cm^{-1} and 28 200–29 000 cm^{-1}. The first group consists of 17 fine lines (region IVa) [$^6A_{1g}\rightarrow{}^4T_{2g}(D)$ transition] and the next one has eight [$^6A_{1g}\rightarrow{}^4E_g(D)$ transition] (region IVb). From temperature variation study it is established that all the bands are of cold origin. A progression of about 110 and 220 cm^{-1} have been observed based on four origins. The intensities of the absorption bands show peculiar behavior, the intensities of some of them (particularly the band at 26 870 cm^{-1} and its associates) drop markedly on rise of temperature following a nonexponential decay typical of the cold magnon sideband. This observation is consistent with previous reports of the appearance of cold magnon sidebands for antiferromagnetically ordered crystals e.g., $CsMnCl_3{\cdot}2H_2O$ (CMC),[17] and MnF_2.[18] At the lowest temperature each of the bands at 26 810 cm^{-1} (373 nm) and 26 870 cm^{-1} (372 nm) has resolved into three fine components separated by ± 2 cm^{-1}. This splitting is attributed to lifting of Kramer's degeneracy due to onset of internal exchange molecular field at low temperature which is brought about by the ordered structure.

To verify how well the assignments of Table II and III agree with the $C_{2h}(a)$ selection rules of Table I, we note the types of polarizations as assigned. In the absorption spectra, transitions to a total of seventeen orthorhombic CF states have been assigned out of which the observed polarization of ten of them (a for five, b,c for four and c for one) are completely consistent with $C_{2h}(a)$ symmetry according to Table I. The observed polarization of seven of them (a,b,c for four, a,b for one, and a,c for two) are consistent with C_i site symmetry, but for C_{2h} would indicate some coincidence of energy levels with different symmetry or perhaps a disguising of orbital symmetry by spin-orbit interactions. The spin-orbit coupling can be expected particularly within the $^4T_{2g}(D)$ states and would make difficult the interpretation of the observed polarizations.

The results of this study compare well with the optical absorption spectra presented for similar Mn^{2+} crystals. The vibrational frequency of 210 cm^{-1} assigned to $A_{1g}\nu$ stretching Mn-Cl mode while the lower frequency of 115 cm^{-1} has been assigned to $A_{1g}\delta$ skeletal bending mode correlates nicely with the observation of 203 and 213 cm^{-1} and 131 and 137 cm^{-1} found in Raman spectra of

CMC.[19] In some cases a slight variation in frequency is observed for the stretching and bending Mn-Cl mode for different excited crystal-field states which is not unusual. The observation of the sideband even at a temperature of 80 K indicates that the exchange interaction is localized to a near neighbor. The failure of observing pure exciton origin prevents us from estimating the magnon dispersion energy. The magnon dispersion of a few cm^{-1} may be a reasonable estimate, as TrMAMC crystal has very low ordering temperature ($T_N \simeq 1$ K); however, in this crystal the magnetic exchange is strongly one dimensional with near neighbor J several times the near chain J', and as T_N is reflected by $(JJ')^{1/2}$, hence an estimate of a few cm^{-1} may be an underestimation. The spectral data for TrMAMC crystal compares well with the spectral features for $[(CH_3)_4N]MnCl_3$-TMMC crystal, both of which have similar chromophore. The similarity between the two studies are (1) the proposed exchange induced mechanism for transition and (2) failure to observe the weak excitonic origin. However the spectra are much better resolved for the TrMAMC crystal and provide an opportunity to look into the lower-symmetry field, a limitation of the previous investigation on TMMC crystal. At the lowest temperature the sharp bands at 26 810 and 26 870 cm^{-1} have shown a fine splitting of 2 cm^{-1}, which is attributed to a lifting of the degeneracy due to the internal molecular field. No such splittings, though theoretically feasible, have been observed for TMMC crystal. However similar splitting due to onset of magnetic field at the lowest temperature have been observed for $CsMnCl_3 \cdot 2H_2O$, single crystal.[13] The separation of 60 cm^{-1} between two lowest Kramer's doublet also agrees with the separation of 70 cm^{-1} for $MnCl_2 \cdot 2H_2O$ single crystal.[20] The high-resolution spectral data for TrMAMC crystal at different temperature and the polarization character have been successful in clearly establishing the orthorhombic nature of the transition site and that a spin-dependent exchange mechanism governs the transition intensity. These characteristics of TrMAMC could not be determined by the previous two optical reports[10,11] on this crystal.

IV. CONCLUSION

The polarized absorption spectra of Mn^{2+} ion in orthorhombic TrMAMC single crystal have been reported at different temperatures. The symmetry of the transition site has been shown to have some remnants of C_{2h}, i.e., higher than true C_i symmetry predicted by crystal structure determination. It is necessary to invoke metal-pair interaction to understand the polarization characteristics of the absorption bands. A total of seventeen orthorhombic CF states are assigned from the polarization of the absorption bands. The weak metal-pair exchange interaction is responsible for distorting the transition site from the approximately tetragonal symmetry expected for the single-ion $MCl_4(H_2O)_2$ chromophore to an approximately orthorhombic one. The localization of the exchange interactions to short range only is postulated from the observation of sidebands at different temperatures. Some anomaly in the polarization of the absorption bands may be due to the occurrence of single-ion process along with ion-pair interaction. Absence of a suitable diagmagnetic host with isomorphous crystal structure prevented us from separating the cooperative absorption phenomena and studying the single-ion process.

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