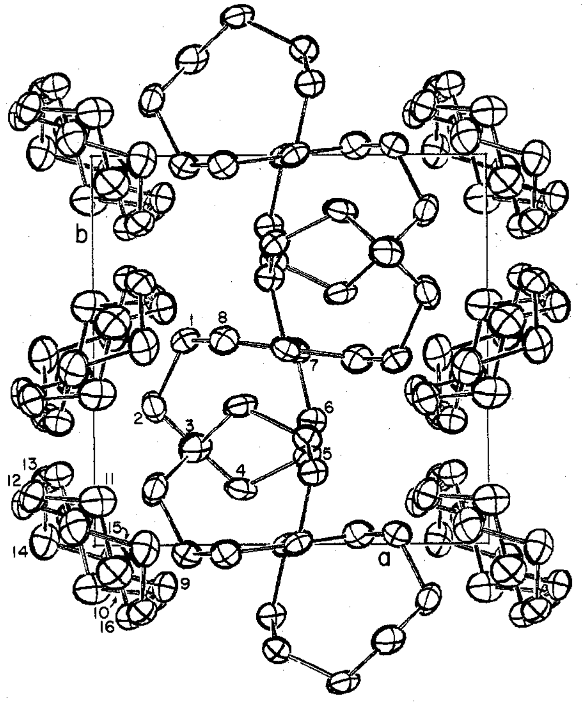

Figure 2. Structure viewed down the *c* axis. The numbered atoms are the same as in Figure 1.

interchange of *a* and *b* would require far greater molecular shifts than occur in the materials which are known to have this property.[13]

We thank a perceptive referee who noticed the special relationship among the coordinates.

Registry No. S_8, 10544-50-0.

Supplementary Material Available: A listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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(1) Work done in part under the auspices of the U.S. Energy Research and Development Administration.
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Physical Properties of Linear-Chain Systems. 4. Optical Spectrum of $RbMnBr_3$[1]

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The compound $RbMnBr_3$ belongs to a class of compounds of general formulation ABX_3 which display predominantly one-dimensional magnetic character.[2] When $A^+ = Cs^+$, Rb^+, or $(CH_3)_4N^+$, B = a divalent first-row transition element, and $X^- = Cl^-$, Br^-, or I^-, these materials crystallize in a hexagonal array of infinite linear chains which are composed of face-sharing BX_6^{4-} octahedra and lie parallel to the *c* crystallographic axis. The chains are separated from one another by the A cations and this separation effectively inhibits interchain exchange. Three-dimensional ordering occurs only at low temperatures while one-dimensional spin correlation is evident at temperatures far above the temperature limit of three-dimensional order.[3-5] The unique nature of these materials is also manifested spectroscopically.[6-8] The absorption spectra exhibit anomalous intensity of spin-forbidden transitions and dependence on temperature incommensurate with that expected for vibronic coupling.

Table I. Observed Maxima, Octahedral Ligand Field Assignments, and Measured Oscillator Strengths in the Spectrum of $RbMnBr_3$ at 4.2 K

Obsd max, cm^{-1}		Assignments (octahedral ligand field states)	Manifold oscillator strengths ($f \times 10^6$)	
$E \parallel c$	$E \perp c$		$E \parallel c$	$E \perp c$
18 149	18 136	$^6A_1(S) \rightarrow {}^4T_1(G)$	0.81	6.44
21 739	21 552	$\rightarrow {}^4T_2(G)$	7.18	8.04
22 995		$\rightarrow {}^4A_1(G)$		
23 063	23 059	$\rightarrow {}^4E(G)$		
23 138		$\rightarrow {}^4A_1 + \nu_{150}$	1.13	0.18
	23 199	$\rightarrow {}^4E + \nu_{140}$		
23 283		$\rightarrow {}^4A_1 + 2\nu_{150}$		
	23 337	$\rightarrow {}^4E + 2\nu_{140}$		
23 364				
26 164	26 161	$^4T_2(D)$	2.41	8.05
~26 360	26 350			
	26 455			
26 504				
26 596	~26 585			
~27 370	27 365	$\rightarrow {}^4E(D)$		
	~27 410			
~27 500	27 510	$\rightarrow {}^4E(D) + \nu_{145}$	0.12	2.44
	~27 555			
~27 650	27 655	$\rightarrow {}^4E(D) + 2\nu_{145}$		
29 498		$\rightarrow {}^4T_1(P)$	0.37	1.05
29 638	29 640			
~29 890	~29 900			
30 030	30 030			
34 602	~34 600	$\rightarrow {}^4A_2(F)$		

To further analyze the properties of these compounds we have measured the polarized, single-crystal absorption spectrum of $RbMnBr_3$ from 300 to 4.2 K.

Experimental Section

Single crystals suitable for spectroscopic measurements were prepared as previously described[6] employing anhydrous RbBr and $MnBr_2$ as starting materials. Polarized spectroscopic measurements were also obtained as before and were made at 300, 150, 120, 100, 80, 60, 40, 30, 20, 15, and 4.2 K. Comparison of σ, π, and axial results showed all observed transitions to be electric dipole in nature. $RbMnBr_3$ was determined to be isomorphous and isostructural with the linear-chain material $CsMnBr_3$ by x-ray photographic techniques.[10]

Results and Discussion

The polarized absorption spectrum of $RbMnBr_3$ at 4.2 K is presented in Figure 1. The gross features of the spectrum can be understood in terms of transitions between the octahedral ligand field states of Mn^{2+}. Assignments on this basis are given with the spectrum in Figure 1. Table I contains the energies of the observed maxima and the oscillator strengths of the absorption manifolds at 4.2 K. Figure 2 presents the variation of oscillator strengths with temperature for those bands which were sufficiently isolated throughout the measured temperature range to permit accurate measurement. The oscillator strengths are normalized with respect to the 4.2-K value. This facilitates comparison between

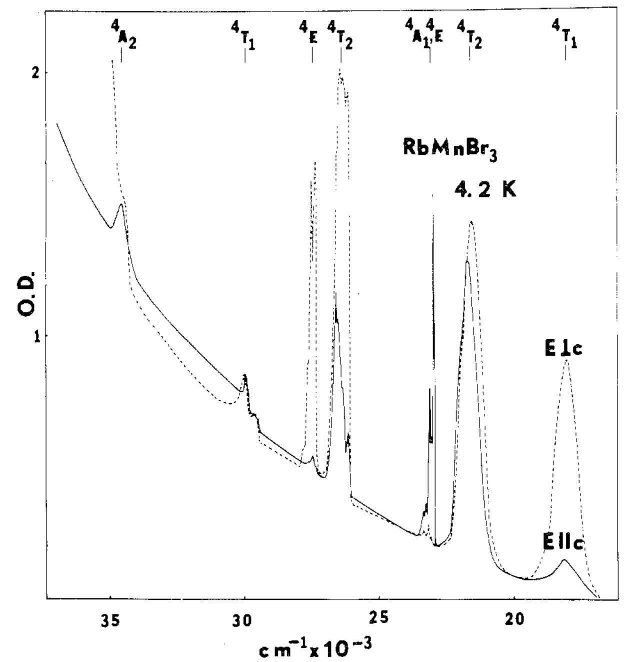

Figure 1. Polarized, single-crystal absorption spectrum of RbMnBr$_3$ at 4.2 K. Octahedral ligand field assignments are included and optical density is in arbitrary units.

experiment and theory and comparison of individual bands.

In the following text the measured absorption bands in the 4.2-K spectrum of RbMnBr$_3$ are discussed independently since distinct physical differences exist.

$^6A_1(S) \rightarrow {}^4T_1(G)$. The absorption associated with this transition appears as a broad, featureless band. An intense maximum is observed at 18 136 cm^{-1} with $E \perp c$ and a weak maximum is observed at 18 149 cm^{-1} with $E \parallel c$. The oscillator strength of the perpendicular component is observed to gradually increase between room temperature and 60 K and then decrease as the temperature is lowered from 60 to 4.2 K, Figure 2. This behavior closely parallels the temperature dependence predicted by Tanabe and co-workers[11,12] for an exchange-induced electric dipole process. Because of the broad, weak nature of the parallel component, no determination of temperature dependence was attempted.

$^6A_1(S) \rightarrow {}^4T_2(G)$. This absorption appears as a broad intense band in both polarizations exhibiting maxima at 21 552 cm^{-1} with $E \perp c$ and at 21 739 cm^{-1} with $E \parallel c$ at 4.2 K. Both components show a gradual increase in oscillator strength between room temperature and 30 K followed by a small decrease between 30 and 4.2 K. Again this behavior is similar to theoretical predictions for an exchange-induced mechanism.

There remains the consideration of the ~200-cm^{-1} difference in band maxima between $E \parallel c$ and $E \perp c$ orientations. This is most likely due to the effect of the trigonal field resultant from the actual D_{3d} site symmetry at the manganese(II) position. This distortion from octahedral is not large and affects the various orbital configurations differently. The $^4T_2(G)$ state is apparently quite sensitive and is split into the $^4A_1$ and ^4E trigonal components. The transition to the $^4A_1$ component is expected to be more allowed with $E \parallel c$ and the transition to the ^4E component more allowed with $E \perp c$. The apparent 200-cm^{-1} separation permits considerable overlap of the oppositely polarized components and they are not independently resolved.

$^6A_1(S) \rightarrow {}^4A_1, {}^4E(G)$. This manifold is observed near 23 000 cm^{-1} and is strongly polarized. With $E \parallel c$ the band is most intense and appears as a strong, sharp peak at 22 995 cm^{-1}, a weak peak at 23 063 cm^{-1}, a strong, sharp, peak at 23 138 cm^{-1}, and shoulders at 23 283 and 23 364 cm^{-1}. With $E \perp c$ the absorption is very weak, exhibiting strongly overlapped maxima at 23 059, 23 199, and 23 337 cm^{-1}. The $E \parallel c$ maxima at 22 995, 23 138, and 23 283 cm^{-1} appear to be components of an ~150-cm^{-1} progression and are completely polarized when $E \perp c$. These are assigned as the $^4A_1(G)$ origin at 22 995 cm^{-1} and two phonon components. The observed weak maxima at 23 059, 23 199, and 23 337 cm^{-1} appear to be components of an ~140-cm^{-1} phonon progression based upon the 23 059-cm^{-1} $^4E(G)$ origin.

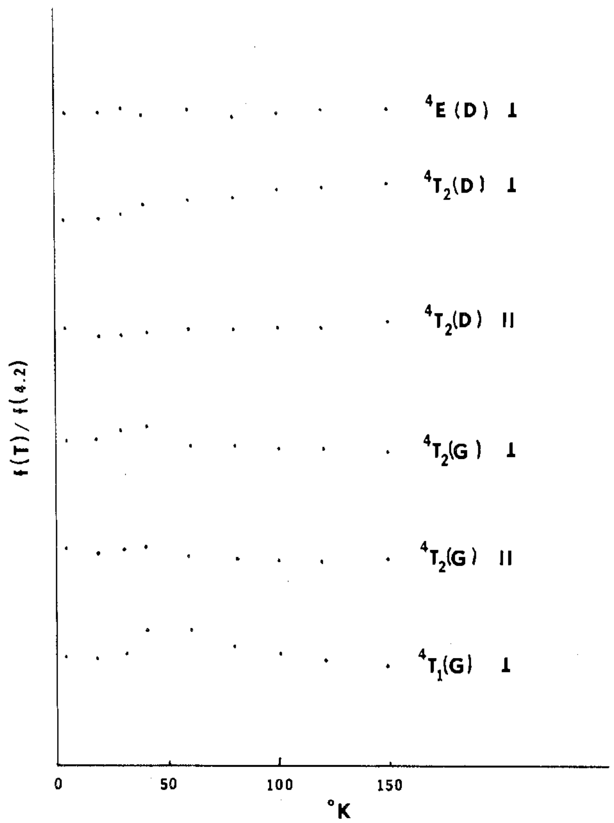

Figure 2. Temperature dependence of the oscillator strengths of selected absorptions in the spectrum of RbMnBr$_3$. Values for an individual band are normalized to the value at 4.2 K. Thus, all 4.2-K values are equal to 1 and are separated for clarity.

$^6A_1(S) \rightarrow {}^4T_2(D)$. The absorption associated with this transition is intense in both polarizations. At 4.2 K, it is most intense with $E \perp c$ and appears as three strongly overlapped maxima at 26 161, 26 350, and 26 455 cm^{-1} followed by a strong shoulder at 26 585 cm^{-1}. With $E \parallel c$ the absorption appears as a weak peak at 26 164 cm^{-1} followed by shoulders at ~26 360 and 26 504 cm^{-1} on the low-energy side of a band centered about a 26 596-cm^{-1} maximum. It is likely that the observed maxima correspond to spin–orbit components, as this state is quite sensitive to spin–orbit coupling.[13] However, the ill-resolved nature of the manifold permits only speculation.

The oscillator strength of the $E \parallel c$ manifold remains constant within experimental error between 150 and 4.2 K. The $E \perp c$ manifold decreases in oscillator strength by ~25% over the same temperature range indicating a vibronic contribution to the total intensity. Room-temperature oscillator strengths were obscured by overlap with the adjacent $^6A_1(S) \rightarrow {}^4E(D)$ absorption.

$^6A_1(S) \rightarrow {}^4E(D)$. At 4.2 K this absorption is most intense with $E \perp c$ and appears as a strong, sharp peak at 27 365 cm^{-1} with a very weak shoulder at ~27 410 cm^{-1} followed by a second strong, sharp peak at 27 510 cm^{-1} with a weak high-energy shoulder at ~27 555 cm^{-1} followed by a strong shoulder at 27 655 cm^{-1}. The maxima at 27 510 and 27 655 cm^{-1} appear to be components of a 145-cm^{-1} progression based on the 27 365-cm^{-1} $^4E(D)$ origin. The weak shoulders are apparently components of the same energy progression based on a false origin or a second spin–orbit component some 45 cm^{-1} above the 27 365-cm^{-1} origin. The oscillator strength of this manifold is constant between 150 and 4.2 K, Figure 2.

With $E \parallel c$ the absorption is very weak and appears as three very weak, strongly overlapped maxima at ~27 370, ~27 500, and ~27 650 cm^{-1}. These appear to be the $E \parallel c$ components of the intense members of the 145-cm^{-1} progression observed with $E \perp c$.

$^6A_1(S) \rightarrow {}^4T_1(P)$. This absorption is most intense with $E \perp c$ and appears as a weak maximum at 29 640 cm^{-1} followed by a more intense manifold exhibiting a shoulder at ~29 890 cm^{-1} and band maximum at 30 030 cm^{-1}. With $E \parallel c$ the absorption is somewhat less intense and appears as a sharp, weak peak at 29 498 cm^{-1}, a weak broad peak at 29 638 cm^{-1}, and a more intense manifold with a shoulder at ~29 890 cm^{-1} and maximum at 30 030 cm^{-1}. This state is quite sensitive to the effect of spin–orbit coupling[13] and to a trigonal field. These effects most likely account for the observed structure but the lack of resolution and absence of clear-cut polarization behavior makes quantitative analysis on this basis impossible.

$^6A_1(S) \rightarrow {}^4A_2(F)$. This absorption appears as a weak shoulder on the charge-transfer absorption with $E \perp c$ and as a pronounced shoulder with $E \parallel c$. In both cases the band is observed at ~34 600 cm^{-1}. The strong overlap with the charge-transfer absorption prevents useful analysis of this absorption.

Summary and Conclusion

While the optical spectrum of $RbMnBr_3$ is superficially that of Mn^{2+} in a trigonally distorted octahedral environment, it displays oscillator strengths which are 2–3 orders of magnitude greater than the analogous transitions in isolated manganese(II) complexes. Comparing the spectrum of $RbMnBr_3$ to the spectrum of the structurally analogous $CsMnBr_3$[6] we note a commonality of polarization behavior. In all cases except where a $^6A_1 \rightarrow {}^4A_1$ transition occurs the more allowed process occurs perpendicular to the chain axis. In the case of the $^6A_1 \rightarrow {}^4A_1$ transitions the sense of polarization is the opposite. Day and Dubicki[7] have derived the selection rules for electronic transitions involving antiferromagnetically coupled Mn^{2+} pairs in TMMC. Since the site symmetry of the Mn^{2+} ions in $RbMnBr_3$ is the same as that for the Mn^{2+} ions in TMMC, the same selection rules apply. These are (for D_{3d} symmetry)

$$^6A_{1g} \xrightarrow{E \parallel c} {}^4A_{1g}$$

$$^6A_{1g} \xrightarrow{E \perp C} {}^4E_g$$

$$^6A_{1g} \nrightarrow {}^4A_{2g}$$

Since states of T_{1g} symmetry in the O_h group become states of $A_{2g} + E_g$ symmetry in the D_{3d} group and since

$$T_{2g} \xrightarrow{D_{3d}} A_{1g} + E_g$$

we should expect one band, allowed $E \perp c$, for the two $^6A_{1g} \rightarrow {}^4T_{1g}$ transitions, Figure 1, and two manifolds for each of the two $^4T_{2g}$ parent states. The behavior of the lowest $^6A_{1g} \rightarrow {}^4T_{1g}$ transitions as well as the behavior of the lowest $^6A_{1g} \rightarrow {}^4E_g$ transition would support the use of the simple pair model selection rules. It is clear however, from the behavior of the $^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$, the $^6A_{1g} \rightarrow {}^4T_{2g}(D)$, the $^6A_{1g} \rightarrow {}^4T_{1g}(P)$, and the $^6A_{1g} \rightarrow {}^4A_{2g}$ transitions that a significant modification of this approach is necessary to accurately describe the spectra of $RbMnBr_3$ and $CsMnBr_3$.

While there are distinct similarities in the band positions and polarization behavior of $RbMnBr_3$ and $CsMnBr_3$, the temperature dependences of the oscillator strengths of corresponding transitions are considerably different. For transitions in the spectrum of $RbMnBr_3$ the temperature dependence that is observed is primarily that predicted by theory[11,12] for an exchange-induced electric dipole process while for $CsMnBr_3$ a variety of temperature dependences is observed some of which possess a distinct vibronic component.

On the basis of the oscillator strengths of corresponding transitions in $RbMnBr_3$ and $CsMnBr_3$, it does not appear, with the limits of our experimental measurements, that the shorter interchain distance and attendant higher T_N in $RbMnBr_3$ in any way affect the transition probability. Indeed in all cases the transitions in the $CsMnBr_3$ system appear to be approximately equal in intensity or stronger. Whether this is, in fact, a general phenomenon or not awaits the investigation of other systems.

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Registry No. $RbMnBr_3$, 38669-02-2.

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Some Metal Halide–Phosphorus Halide–Alkyl Halide Complexes. 4. Bis(*tert*-butyltrichlorophosphonio)tri-μ-chloro-hexachloro-*triangulo*-trirhenium(III) Hexachlororhenate(IV)

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The reaction of a metal halide with a *tert*-butyl halide and a phosphorus(III) halide has been used[2-4] to synthesize the anions BCl_4^-, $AlCl_4^-$, $SnCl_5^-$, $NbCl_6^-$, $TaCl_6^-$, WCl_6^-, $Ti_2Cl_9^-$, $Ti_2Br_9^-$, and $Zr_2Cl_9^-$. The analogous reaction for rhenium(V) chloride is now presented in which a single compound containing the tri-μ-chloro-hexachloro-*triangulo*-trirhenium(III) unit, the hexachlororhenate(IV) anion, and the *tert*-butyltrichlorophosphonium cation is formed. Previously bromides[5] containing both Re_3Br_9 and $ReBr_6^{2-}$ have been reported.

Experimental Section

Rhenium(V) chloride (99.5%) was used as supplied and other reagents were as previously described.[2]