

tures centered at 15 400 and 15 680  $\text{cm}^{-1}$  in the solution CD to  ${}^4A_2 \rightarrow {}^2T_1$  transitions. Our single-crystal experiments show that this is an unlikely assignment because it neglects the large contribution to the CD from the (totally symmetric) vibronic  ${}^4A_2 \rightarrow {}^2E$  transitions. It is also in disagreement with the theoretical prediction that  $R({}^4A_2 \rightarrow {}^2T_1)$  is smaller than  $R({}^4A_2 \rightarrow {}^2E)$  by at least a factor of 3.<sup>13,15</sup>

The negative peak in the solution CD centered at 15 420  $\text{cm}^{-1}$  more or less coincides with the maximum of positive CD in the axial spectrum.  $\pi$ -Polarized transitions obviously determine the sign in this region. The same is not true in the

region of electronic origins  ${}^4A_2 \rightarrow {}^2E$  (14 900  $\text{cm}^{-1}$ ), where the sign of the CD is determined by the axial transitions. If solvent effects can be neglected there must be  $\pi$ -polarized transitions in the 15 420-  $\text{cm}^{-1}$  region with larger  $R/D$  ratios than the corresponding electronic origins.

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**Registry No.** [(+)<sub>D</sub>-Cr(en)<sub>3</sub>]Cl<sub>3</sub>, 30983-64-3; 2[Cr(en)<sub>3</sub>Cl<sub>3</sub>]·KCl, 54293-11-7.

Contribution from the Department of Chemistry,  
University of Michigan, Ann Arbor, Michigan 48109

## Electronic Spectroscopy of Nearly Octahedrally Coordinated Manganese in MnPS<sub>3</sub> and CdPS<sub>3</sub> Lattices

J. BOERIO-GOATES, E. LIFSHITZ, and A. H. FRANCIS\*

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The phosphorescence and phosphorescence excitation spectra of octahedrally coordinated d<sup>5</sup> manganese in MnPS<sub>3</sub> and CdPS<sub>3</sub> lattices have been recorded at 77 K and at 4 K. The phosphorescence lifetime of the  ${}^4T_1 \rightarrow {}^6A_1$  emission in MnPS<sub>3</sub> is indicative of rapid energy transfer from excited manganese ions to nonradiative trapping sites. Analysis of the excitation spectra of CdPS<sub>3</sub>:Mn (1%) suggests that the Mn<sup>2+</sup> ions may both substitutionally replace Cd<sup>2+</sup> ions in the host lattice and occupy octahedral sites in the van der Waals gap. Additionally, there is evidence for rapid energy exchange between electronically excited cadmium and manganese ions. The electronic excitation spectra of Mn<sup>2+</sup> ion in MnPS<sub>3</sub> differ dramatically from all previously reported spectra of octahedrally coordinated d<sup>5</sup> manganese and suggests an exceptionally large value of the ligand field splitting parameter  $10Dq/B$ . The electronic excitation spectra are interpreted in the strong crystal field scheme with use of the Tanabe-Sugano energy matrices. Excellent agreement with the experimental spectroscopic data is obtained with use of a crystal field splitting parameter  $10Dq = 8750 \text{ cm}^{-1}$  values of the Racah parameters  $B = 494 \text{ cm}^{-1}$  and  $C = 3349 \text{ cm}^{-1}$ . The intensity maximum of  ${}^4T_1 \rightarrow {}^6A_1$  phosphorescence in MnPS<sub>3</sub> is observed at 9250 Å and is therefore the longest wavelength Mn<sup>2+</sup> emission to have been reported.

### Introduction

Many transition-metal chalcogenophosphates (MPS<sub>3</sub>) crystallize in a layered structure in which parallel planes of transition-metal ions are separated by two planes of sulfur atoms. The structure of the MPS<sub>3</sub> compounds has been reported in detail only for FePS<sub>3</sub><sup>1</sup> which belongs to the C<sub>2h</sub><sup>3h</sup> monoclinic space group with 2 formula units per unit cell. Each transition-metal ion is surrounded by six sulfur atoms forming a trigonally distorted octahedron. MnPS<sub>3</sub> and CdPS<sub>3</sub> belong to the same monoclinic system as FePS<sub>3</sub> and have closely similar lattice parameters.<sup>2</sup> One may assume that the structures of all three materials are isomorphous.

In the layered MPS<sub>3</sub> structure, adjacent planes of sulfur atoms are weakly bonded by van der Waals interactions, and a variety of well-defined intercalation compounds may be formed by introduction of atoms, ions, and molecules into the van der Waals gap between the adjacent sulfur planes. The intercalation reactions of MPS<sub>3</sub> compounds are reversible, topotactic solid-state reactions in which a mobile guest species enters the solid host lattice. The intercalated species is evidently weakly bonded and, in some cases, dynamically disordered at room temperature. The physical properties of many MPS<sub>3</sub> compounds such as transport phenomena, superconductivity, magnetic and optical properties, phase transitions, etc. may be modified significantly by intercalation.<sup>3</sup>

The lamellar structure of the MPS<sub>3</sub> materials leads to highly two-dimensional behavior in many of their physical properties.

Measurements indicate a 10<sup>5</sup> greater electron mobility intraplane than interplane. The temperature dependence of the magnetic susceptibility indicates that these compounds are two-dimensional Heisenberg antiferromagnets below about 100 K.<sup>4</sup> Intercalation with organometallic compounds leads to a decrease in the two-dimensional Heisenberg exchange interaction and a corresponding decrease in the Néel temperature of the material.<sup>4</sup> Similarly, intercalation also leads to a decrease in the superconducting critical temperature.<sup>5</sup> Thus, intercalation generally decreases the intraplane exchange interactions between transition-metal ions. The Heisenberg exchange interaction ultimately depends upon the overlap of transition-metal orbitals on adjacent sites and is therefore similar in nature to the exchange interaction leading to exciton and magnon migration in the excited state. We anticipate that exciton energy transport may also be affected by intercalation.

The lamellar nature of these materials and the relatively large interplanar spacing (van der Waals gap) between adjacent sulfur atom layers makes this class of materials particularly useful for the study of energy migration and energy exchange in solids. These compounds may serve as highly two-dimensional materials for the study of exciton migration and may ultimately provide experimental data with which to test existing theories for diffusive, percolative, and hopping exciton migration in two-dimensional lattices. For a comparison of experimental data with the theoretical predictions based on different models for the macroscopic averaging of energy migration, it is necessary that the dimensionality of

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the lattice be well defined. Transition-metal salts of the general formula  $A_2XY_3$ , where  $A = Na, K, \text{ or } Cs$  and  $Y = Cl \text{ or } Br$ , have been demonstrated to be highly one-dimensional both in their magnetic behavior and in their dielectric properties. Studies of exciton migration in these materials have demonstrated that general agreement with exciton migration by a one-dimensional hopping model may be obtained.<sup>6</sup> It may be anticipated that the two-dimensional materials discussed in the present work will be similarly useful in further exploring the relationship between lattice dimensionality and exciton migration.

Additionally, the possibility of the formation of intercalation compounds with a wide variety of organic, inorganic, and organometallic compounds as well as certain metal atoms and ions lends a further dimension to the possible experimental studies. By intercalation of species with states lying above or below the exciton band of the transition-metal array, it may be possible to observe energy-transfer processes both within and between the metal ion planes.

Unfortunately, the majority of chalcogenide intercalation compounds have been characterized only by analytical composition and by determination of the interlayer spacing from X-ray powder diffraction. It has been noted that the lack of characterization as regards reproducible synthesis, composition, structure, and bonding constitutes a severe problem currently in intercalation chemistry.<sup>3</sup> Historically, vibrational and electronic spectroscopy have been of considerable utility in the characterization of materials. It is the purpose of this paper to report the results of preliminary investigations of the electronic spectra of manganese in several  $MPS_3$  lattices in order to provide the necessary experimental data for subsequent studies of intercalation compounds of these materials.

### Experimental Section

**Sample Preparation.** Single crystals of pure  $MnPS_3$  were prepared with use of the vapor sublimation method described by Taylor et al.<sup>7</sup>  $Mn^{2+}$ -doped  $CdPS_3$  crystals were also synthesized with use of this method. The synthesis of  $MnPS_3$  was accomplished by heating a stoichiometric mixture of the constituent elements in an evacuated fused silica tube in a vertical two-zone furnace where a 750–690 °C temperature gradient was established over 30 cm. A good yield of crystals in the form of platelets could be obtained after heating in this manner for 7–10 days.

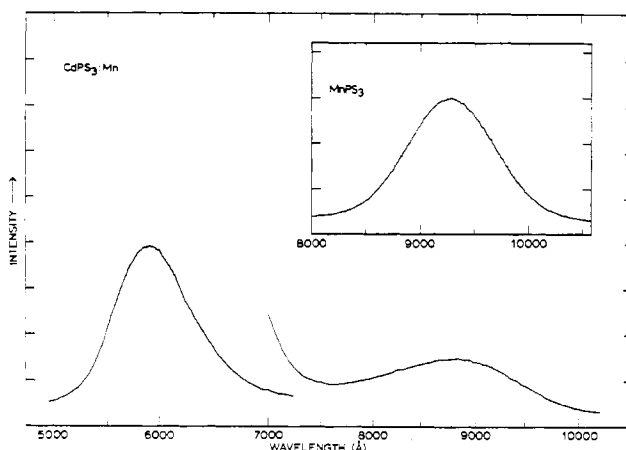
In the preparation of the Mn-doped samples, sufficient metallic manganese was added to the mixtures to give an initial 1 mol % concentration. A temperature gradient of 670–600 °C was used in the preparation of the cadmium sample.

Elemental analyses of the  $MnPS_3$  (% Mn = 30.47, % P = 16.34, % S = 52.94) and  $CdPS_3$  (% Cd = 45.89, % P = 12.24, % S = 41.83) crystals prepared by the above methods were in substantial agreement with the empirical formulas.

**Electronic Spectra.** The phosphorescence and phosphorescence excitation spectra of  $CdPS_3:Mn$  and  $MnPS_3$  were determined with use of single-crystal samples of approximate dimensions  $0.1 \times 5 \times 5$  mm. The crystals were mounted in a Janis Model 10DT cryostat and cooled by a flow of helium vapor from a liquid helium reservoir.

Sample luminescence was excited with the broad band emission from a high-pressure 1-kW xenon arc lamp, filtered by a cupric sulfate solution. The emission was dispersed with a 1-m Interactive Technology monochromator and detected with a cooled RCA 7102 photomultiplier tube.  $MnPS_3$  emission was filtered with a Corning 2-62 filter placed before a monochromator entrance slit to eliminate light reflected from the surface of the crystal. Corning 2-58 and 3-70 filters allowed study of the manganese emission from the doped crystal samples.

Because of the weak intensity and broad line shape of manganese emission, excitation spectra were recorded by monitoring the total sample luminescence unless otherwise noted. The excitation source employed was 1-kW xenon arc lamp which was monochromated by a half-meter  $f/9$  scanning monochromator operated with a 25-Å



**Figure 1.** Phosphorescence spectrum of single-crystal  $CdPS_3:Mn$  recorded at approximately 4.2 K. Phosphorescence spectrum of single-crystal  $MnPS_3$  recorded at approximately 4.2 K is given in the insert.

band-pass. A Corning 7-56 filter was utilized to isolate  $MnPS_3$  emission, and a Corning 2-58/7-59 filter combination was used to pass the manganese emission from doped  $CdPS_3$  crystals.

The lifetime measurements were made with use of a xenon flash lamp with a 7- $\mu s$  decay time. The exciting light was filtered through a cupric sulfate solution while the emission was filtered with a Corning 2-62 filter. The signal was processed with a Northern digital signal averager; the decay curves were found to be exponential with time.

**Photoconductivity Measurements.** Single crystals of  $MnPS_3$  approximately  $0.1 \times 5 \times 5$  mm in size were selected for photoconductivity measurements. Electrical contact was made by indium soldering No. 40 copper wire leads directly to the crystal. The crystals were too thin to permit measurement of the photoconductivity perpendicular to the principal cleavage plane. The wavelength dependence of the photoconductivity was determined by irradiation of the sample with nearly monochromatic light which was amplitude modulated by a mechanical chopper. The photocurrent was measured with a Keithley Model 603 electrometer with  $10^{14}$ - $\Omega$  input impedance. The amplitude modulated component of the photocurrent was detected with the aid of a phase-sensitive synchronous amplifier.

### Discussion

The electronic absorption and emission spectra of  $Mn^{2+}$  have been extensively investigated in a wide variety of compounds. The excitation and emission spectra of  $Mn^{2+}$  in  $MnPS_3$  and  $CdPS_3$  differ from the spectra of  $Mn^{2+}$  in previously studied lattices in that both the characteristic absorption bands and the emission band are dramatically shifted to longer wavelengths. For example, an emission maximum at about 6000 Å is fairly characteristic of manganese when either tetrahedrally or octahedrally coordinated. The manganese emission maximum in  $MnPS_3$  at 9250 Å is shifted to longer wavelengths by 3250 Å. The compounds which most resemble  $MnPS_3$  in their electronic spectra are  $MnS^8$  and  $MnO^9$ . The electronic spectra of these materials show several bands shifted to longer wavelengths relative to their positions in more ionic compounds such as  $MnF_2$ .

The emission spectrum of  $Mn^{2+}$  in  $MPS_3$  lattices is at a much longer wavelength than observed in any manganese compound previously investigated and most closely resembles the phosphorescence of  $Mn^{2+}$  in GaP where manganese substitutionally replaces Ga with nearly tetrahedral phosphorus coordination.<sup>10</sup> The phosphorescence of  $Mn^{2+}$  in GaP is the longest wavelength manganese emission previously reported ( $\lambda_{max} = 9000$  Å).

**$MnPS_3$  Phosphorescence Spectrum.** The emission spectrum of single crystals of  $MnPS_3$  is shown in the insert of Figure

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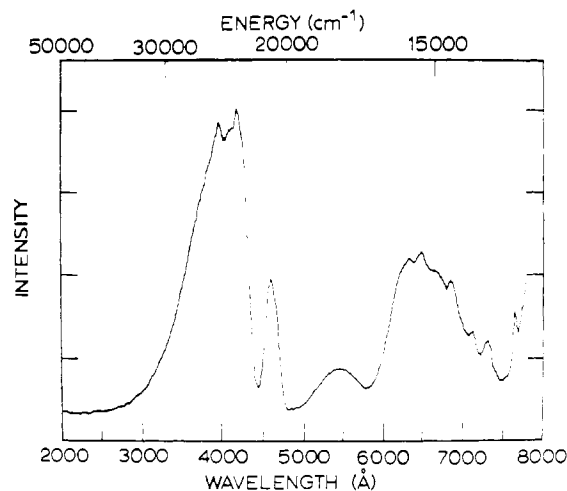


Figure 2. Phosphorescence excitation spectrum of single-crystal MnPS<sub>3</sub> recorded at approximately 4.2 K.

1 and consists of a single broad, featureless band centered at 9250 Å. Emission intensity increases substantially as the temperature is decreased to 4.2 K with no apparent change in either the shape or peak position.

**MnPS<sub>3</sub> Phosphorescence Excitation Spectrum.** The phosphorescence excitation spectrum of MnPS<sub>3</sub> obtained by monitoring the entire phosphorescence band centered at 9250 Å is shown in Figure 2. Although several strong absorption bands are expected in the 2000–3000-Å spectral range, no bands were observed in the excitation spectrum in this region. Evidently, excitation wavelengths shorter than about 3000 Å do not lead to population of the <sup>4</sup>T<sub>1</sub>(<sup>4</sup>G) state. This may be attributed to electron-hole excitation and relaxation by carrier recombination. We have determined the wavelength dependence of the photoconductivity of MnPS<sub>3</sub>, and the results shown in Figure 3 are consistent with this interpretation. The semiconducting band gap of MnPS<sub>3</sub> was determined to be about 3 eV.

The excitation spectrum of MnPS<sub>3</sub> which lies to longer wavelengths than 3000 Å is qualitatively similar to that of Mn<sup>2+</sup> in MnO and MnS and may be interpreted within the framework of the strong crystal field splitting model. The energy levels of Mn<sup>2+</sup> in a cubic crystalline field have been calculated by Tanabe and Sugano in terms of the Racah parameters *B* and *C* and the crystal field splitting parameter *10Dq*.<sup>11</sup> The octahedral crystal field mixes only states of symmetry T<sub>1</sub> arising from the free ion terms <sup>4</sup>P, <sup>4</sup>F, and <sup>4</sup>G and states of symmetry T<sub>2</sub> arising from <sup>4</sup>F, <sup>4</sup>G, and <sup>4</sup>D. States of symmetry A<sub>1</sub>, A<sub>2</sub>, and E are not mixed by the octahedral crystal field and are therefore *10Dq* independent. The appropriate energy matrices for the mixing of <sup>4</sup>T<sub>1</sub> states and <sup>4</sup>T<sub>2</sub> states are given by Tanabe and Sugano and are reproduced below. The inclusion of the Trees<sup>12</sup> correction term has been reported to substantially improve the agreement between the calculated and experimental energies for Mn<sup>2+</sup> in ionic lattices.<sup>13</sup> The Trees parameter  $\alpha$  has been added to the Tanabe-Sugano energy matrices as shown in Chart I.

The phosphorescence excitation spectrum of MnPS<sub>3</sub> (Figure 2) may be interpreted with the aid of the Tanabe-Sugano energy matrices for octahedrally coordinated manganese. The sharp feature in the excitation spectrum at 4610 Å is attributed to the transition <sup>4</sup>E(<sup>4</sup>G) ← <sup>6</sup>A<sub>1</sub> which is *Dq* independent. This characteristically sharp feature of the spectrum is readily

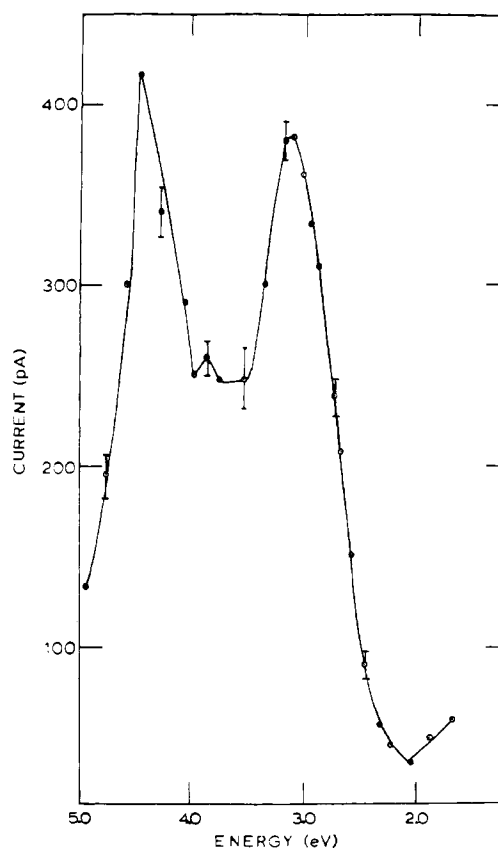


Figure 3. Wavelength dependence of the photocurrent in single-crystal MnPS<sub>3</sub>, recorded at 300 K.

Chart I

<sup>4</sup>T<sub>1</sub>

<sup>4</sup> P	<sup>4</sup> F	<sup>4</sup> G
-10Dq-25B +6C +12α	-3√2B -2√2α	C -8α
	-16B+7C + 10α	-3√2B -2√2α
		10Dq-25B +6C +12α

<sup>4</sup>T<sub>2</sub>

<sup>4</sup> F	<sup>4</sup> G	<sup>4</sup> D
-10Dq-17B+12α	√6B -2√6α	C
	-22B+5C+14α	-√6B + 2√6α
		10Dq-17B +6C + 12α

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identified and is found at 4630 Å in the spectrum of octahedrally coordinated Mn<sup>2+</sup> in the cubic MnS lattice.<sup>8</sup> The <sup>4</sup>A<sub>1</sub>(<sup>4</sup>G) ← <sup>6</sup>A transition, which is also *Dq* independent and at 4664 Å for Mn<sup>2+</sup> in hexagonal ZnS,<sup>8</sup> is expected to lie to

Table I

Mn <sup>2+</sup> in:	B, cm <sup>-1</sup>	C, cm <sup>-1</sup>	10Dq, cm <sup>-1</sup>	ref
free ion	786	3790		
MnO	786	3210	9790	9
Mn(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>	671	3710	8480	15
MnCl <sub>2</sub> ·2H <sub>2</sub> O	630	3600	8000	16
MnBr <sub>4</sub> <sup>2+</sup>	536	3530	3100	17
MnS	583	3125	7300	8
MnPS <sub>3</sub>	494	3349	8750	

higher energy, but slightly below its free ion value due to the usual reduction in the Racah parameters  $B$  and  $C$ . The  ${}^4E({}^4D) \leftarrow {}^6A_1$  transition is confidently assigned to the sharp feature at approximately 3980 Å. The corresponding feature in the spectrum of ZnS:Mn is found at 3918 Å. With these assignments made, it is possible to compute the values of the Racah parameters  $B$  and  $C$  for the octahedrally coordinated Mn<sup>2+</sup> ion. Relative to the  ${}^6A_1$  ground state, the energies of the  ${}^4E({}^4G)$  and  ${}^4E({}^4D)$  states in terms of the parameters  $B$  and  $C$  are  $10B + 5C = E[{}^4E({}^4G)]$  and  $17B + 5C = E[{}^4E({}^4D)]$ . Thus, we obtain  $B = 494 \text{ cm}^{-1}$  and  $C = 3349 \text{ cm}^{-1}$ .

For the value of the crystal field splitting parameter  $10Dq$  to be obtained, the full matrices of Tanabe and Sugano were diagonalized over a range of  $10Dq$  values from 0 to 10000 cm<sup>-1</sup> and the best fit made to the remaining features of the observed spectrum. The results of this computation and the best fit to the experimental data with  $\alpha = 0$  are shown in Figure 4. The corresponding value of  $10Dq$  is 8750 cm<sup>-1</sup>. A poorer fit to the experimental data is obtained with use of a value of the Trees parameter  $\alpha = 76$ . The corresponding values of the Racah parameters and the crystal field splitting parameter are then  $B = 638 \text{ cm}^{-1}$ ,  $C = 2763 \text{ cm}^{-1}$ , and  $10Dq = 7650 \text{ cm}^{-1}$ . The results of this computation and the fit to the experimental data obtained are also illustrated in Figure 4. The results of the crystal field calculation are summarized in Table I where the parameters obtained are compared with values of  $B$ ,  $C$ , and  $10Dq$  obtained from several other manganese salts.

The data assembled in Table I demonstrate that the values of the crystal field splitting parameter  $10Dq$  obtained from MnPS<sub>3</sub> are fairly typical of those found in a variety of other manganese compounds. However, the value of the Racah  $B$  parameter is dramatically reduced from its free ion value, well below its usual value in other manganese compounds. The reduction in  $B$  leads to an exceptionally large value of the ratio of  $10Dq/B$  and is the predominate cause of the pronounced long wavelength shifts of the absorption bands in the spectrum of MnPS<sub>3</sub>. The reduction of  $B$  may be attributed to a high degree of covalent bonding between manganese and the six sulfur ligands in MnPS<sub>3</sub> lamellar compounds. This view is consistent with the failure of the Trees correction parameter to improve the theoretical fit to the experimental data. The success of the Trees correction technique is greatest when coordination is more ionic; in instances where highly covalent bonding is involved, the Trees correction frequently results in a poorer fit.<sup>14</sup>

**Energy Transfer in MnPS<sub>3</sub>.** The phosphorescence life time determined for several MnPS<sub>3</sub> crystals synthesized and grown separately was found to vary substantially from one crystal to the next. Typically, half-lives were on the order of 50 μs at 77 K and increased about 10% as the temperature was decreased to 4.2 K. The temperature dependence of both the intensity and life time of  ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$  phosphorescence

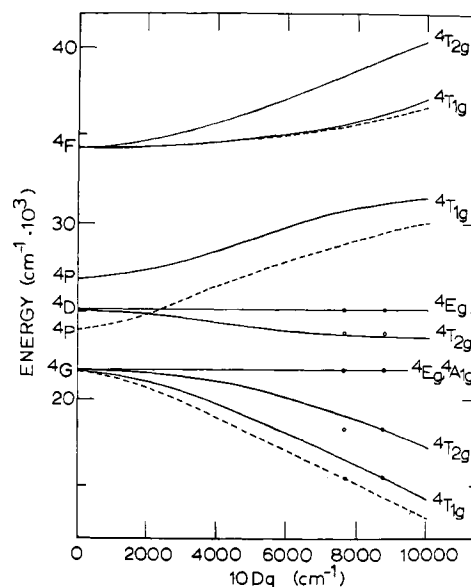


Figure 4. Splitting of Mn<sup>2+</sup> free-ion terms by an octahedral crystal field. Solid curves were computed for  $B = 494 \text{ cm}^{-1}$ ,  $C = 3349 \text{ cm}^{-1}$ , and  $\alpha = 0$ . The dashed curves show the shifts resulting from  $B = 638 \text{ cm}^{-1}$ ,  $C = 2763 \text{ cm}^{-1}$ , and  $\alpha = 76$ . Circles indicate position of experimentally determined energy levels and approximate uncertainty in energy.

is consistent with rapid and efficient thermally assisted energy transfer from excited manganese ions to nonradiative traps. The activation energy for this process in MnPS<sub>3</sub> is evidently sufficiently low that trapping remains competitive with manganese radiative decay even at 4.2 K.

The radiative lifetime and its temperature dependence may be compared with that of Mn<sup>2+</sup> in a variety of other materials. In the three-dimensional crystals MnF<sub>2</sub>, KMnF<sub>3</sub>, and K<sub>2</sub>MnF<sub>4</sub>, radiative life time is determined almost entirely by quenching by nonradiative traps in this temperature range. Exciton migration in three-dimensional materials is extremely efficient even at 2 K, and small concentrations of nonradiative quenching transition-metal ions are difficult to remove. Exciton dynamics in a nominally pure crystal of MnF<sub>2</sub> were investigated by MacFarlane and Luntz<sup>18</sup> and by Wilson et al.<sup>19</sup> A small concentration of Mg<sup>2+</sup> and Ca<sup>2+</sup> traps established the trapping time in the sample studied at 250 μs at 1.9 K. McClure and co-workers determined that manganese excitons migrate rapidly in the one-dimensional material (CH<sub>3</sub>)<sub>4</sub>N-MnCl<sub>3</sub> (TMMC) at temperatures above 77 K.<sup>20</sup> Free excitons are effectively trapped by Co<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup>. In both TMMC and MnF<sub>2</sub>, exciton motion is thermally assisted. A substantial distortion is expected to accompany excitation to the  ${}^4T_1$  state, resulting in a self-trapping of the free exciton. It is necessary, therefore, for lattice phonons to participate in thermalization of the localized exciton. Thus, in both materials, an increase in the rate of trapping and a corresponding decrease in the manganese radiative life time is observed with increasing temperature. McClure and co-workers observed an activation energy for quenching of 420 cm<sup>-1</sup> in TMMC. Similar behavior was observed by McPherson and Francis in the one-dimensional salt CsMnBr<sub>3</sub>.<sup>6</sup>

**Energy Transfer in CdPS<sub>3</sub>:Mn.** The emission spectra of single crystals of CdPS<sub>3</sub> doped with 1 mol % of Mn<sup>2+</sup> exhibited two broad bands centered at 5800 and 8800 Å as shown in Figure 1. Excitation spectra could be obtained monitoring each

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emission band separately. The principal feature of the excitation spectrum obtained monitoring the 5800-Å emission is a relatively sharp band at 4200 Å. The 8800-Å emission band was obtained with excitation wavelengths shorter than the CdPS<sub>3</sub> absorption edge at 3500 Å.<sup>21</sup>

The emission band at 5800 Å is characteristic of either octahedrally or tetrahedrally coordinated Mn<sup>2+</sup> ion in a wide variety of lattices. For example, tetrahedral coordination of Mn<sup>2+</sup> in ZnS produces a strong <sup>4</sup>T<sub>1</sub>(<sup>4</sup>G) → <sup>6</sup>A<sub>1</sub>(<sup>6</sup>S) phosphorescence with λ<sub>max</sub> at 5800 Å. The opportunity for both octahedral and tetrahedral sulfur coordination may be found within the van der Waals gap of MPS<sub>3</sub> lattice with the FePS<sub>3</sub> structure.

Moreover, lamellar compounds, and particularly the chalcogenides, can easily be nonstoichiometric due to a metal excess in the van der Waals gap. These metal ions will link the transition-metal planes and have been shown to hinder diffusion and related motions of the planes.<sup>3</sup> Therefore, we infer that the 5800-Å emission obtained from CdPS<sub>3</sub>:Mn is due to octahedrally or tetrahedrally sulfur-coordinated Mn<sup>2+</sup> ions intercalated between the sulfur planes. The single sharp band observed at 4200 Å in the 5800-Å excitation spectrum may then be plausibly assigned to the <sup>4</sup>E(<sup>4</sup>G) → <sup>6</sup>A<sub>1</sub>(<sup>6</sup>S) transition, which is observed at 3920 Å in ZnS:Mn (wurtzite).<sup>8</sup>

The emission band observed at 8800 Å is similar to that observed in MnPS<sub>3</sub> and therefore attributed to Mn<sup>2+</sup> ions which have substitutionally replaced Cd<sup>2+</sup> in the CdPS<sub>3</sub> lattice. No Mn<sup>2+</sup> bands could be observed in the excitation spectrum obtained monitoring the 8800-Å emission; therefore, the manganese emission at 8800 Å is excited, at least predominantly, by excitation of the host CdPS<sub>3</sub> lattice above the strong absorption edge at 3500 Å. Since no emission at 5800 Å could be obtained by excitation above the CdPS<sub>3</sub> absorption edge, we conclude that there is rapid and efficient energy transfer within the two-dimensional metal ion planes but essentially no energy transfer from the metal ion plane to intercalated manganese ions. Moreover, since *direct* excitation of the substitutional and intercalated manganese centers should lead to emission with about equal efficiency, we must also conclude that the larger portion of the manganese content of the doped

CdPS<sub>3</sub> crystals is intercalated between the sulfur planes.

An additional weak green luminescence band with peak intensity at 5200 Å could be excited by irradiating CdPS<sub>3</sub>:Mn in a narrow band with λ<sub>max</sub> ≈ 3100 Å. Identical luminescence and excitation bands may be observed in nominally pure ZnS and CdS crystals.<sup>14,22</sup> The center responsible for these emission and excitation spectra can be correlated with isolated Zn and Cd neutral atoms occupying interstitial positions in the crystal lattice. The excitation and emission transitions are correlated with the <sup>1</sup>P<sub>1</sub> ← <sup>1</sup>S<sub>0</sub> and <sup>3</sup>P<sub>2,1</sub> → <sup>1</sup>S<sub>0</sub> atomic transitions, respectively. Therefore, the spectroscopic evidence indicates the presence of some metallic cadmium in our sample material.

**Conclusion.** The phosphorescence excitation spectra of Mn<sup>2+</sup> in MnPS<sub>3</sub> and CdPS<sub>3</sub>:Mn have been recorded and compared with the spectra of Mn<sup>2+</sup> in related manganese compounds. The observed electronic excitation and emission spectra, although at markedly longer wavelength than those in Mn<sup>2+</sup> in any other lattice, may be interpreted in terms of the conventional octahedral crystal field splitting of the free ion <sup>4</sup>G and <sup>4</sup>D terms. The crystal field splitting parameter 10Dq for MnPS<sub>3</sub> is of comparable magnitude to that for MnS. Since the crystal field splitting parameter is relatively unchanged from its value in MnS, the long wavelength shift of the spectrum of MnPS<sub>3</sub> must be attributed to the reduction in the magnitude of the Racah B parameter which is due to the high-order covalent bonding between manganese and the sulfur ligands.

Spectroscopic evidence is presented for rapid electronic energy transfer from Cd<sup>2+</sup>-donor to Mn<sup>2+</sup>-acceptor sites in CdPS<sub>3</sub>:Mn. Additionally, spectroscopic evidence suggests that Mn<sup>2+</sup> ions, in addition to substitutionally replacing octahedrally coordinated Cd<sup>2+</sup> ions in the transition-metal plane, may also occupy octahedrally or tetrahedrally sulfur-coordinated sites in the van der Waals gap. Further work is currently in progress to investigate the effect on energy transfer of intercalation by organic cations.

**Registry No.** MnPS<sub>3</sub>, 59707-74-3; CdPS<sub>3</sub>, 60495-79-6.

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