[8] A. S. Alekseev, T. A. Astemirov, V. S. Bagaev, T. I. Galkina, N. A. Penin, N. N. Sibeddin, and V. A. Tsvetkov, in *Proceedings of the Twelth International Conference on the Physics of Semiconductors, Stuttgart, 1974,* edited by M. H. Pilkuhn (B. G. Teubner, Stuttgart, Germany, 1974), p. 94.

[9] J. P. Wolfe, R. S. Markiewicz, S. M. Kelso, J. E. Furneaux, and C. D. Jefferies, Phys. Rev. B 18, 1479 (1978). The lifetimes measured by these authors for an e-h drop in a deep strain well and under very low excitation power are slightly shorter than those measured by us.

[10] L. Liu, Solid State Commun. 25, 805 (1978).

[11] B. J. Feldman, H.-h. Chou, and G. K. Wong, Solid State Commun. 26, 209 (1978).

[12] J. C. Hensel and K. Suzuki, Phys. Rev. B 9, 4219 (1974); I. Balslev, Phys. Rev. 143, 636 (1966).

[13] J. M. Worlock, T. C. Damen, K. L. Shaklee, and J. P. Gordon, Phys. Rev. Lett. 33, 771 (1974); Y. E. Pokrovskii and K. E. Svistunova, Pis'ma Zh. Eksp. Teor. Fiz. 13, 297 (1971) [JETP Lett. 13, 212 (1971)].

[14] T. M. Rice, Bull. Am. Phys. Soc. 20, 470 (1975).

[15] J. C. Hensel, T. G. Phillips, and T. M. Rice, Phys. Rev. Lett. 30, 227 (1973).

[16] R. Conradt and W. Waildelich, Phys. Rev. Lett. 20, 8 (1968).

[17] R. F. Leheny, J. Shah, and M. Voos, Solid State Commun. 20, 819 (1976).

[18] Under stress the binding energy of the drop decreases significantly from its zero-stress value. Even for a drop of size 30 μm, thermionic emission will limit the lifetime to a value much shorter than that measured.

[19] D. L. Smith, M. Chen, and T. C. McGill, Solid State Commun. 18, 1485 (1976); D. L. Smith and T. C. McGill, Phys. Rev. B 14, 2448 (1976).

Extensive Energy Transfer in a Nearly One-Dimensional Crystal: The Emisson Spectrum of $CsMnBr_3$ Doped with Nd^{3+}

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Crystals of a nearly one-dimensional salt, $CsMnBr_3$, which have been doped with trivalent neodymium, exhibit emissions from both Nd^{3+} and Mn^{2+}. At room temperature the emission from Nd^{3+} is strikingly intense, much stronger than the Mn^{2+} emission. It appears that the manganese excitation migrates rapidly along the anionic chains in $CsMnBr_3$ and is trapped by the Nd^{3+} impurities. As the temperature is lowered, the rate of energy migration decreases and the Mn^{2+} emission grows at the expense of the Nd^{3+} emissions. There appears to be little energy transfer below 40 K.

Crystals of $CsMnBr_3$ which have been doped with trivalent neodymium luminesce strongly when excited by visible or uv radiation ($\lambda < 600$ mm). The emission spectrum contains features which can be attributed to both Nd^{3+} and Mn^{2+}. Although the concentration of Nd^{3+} in the doped crystals is relatively low (on the order of 1 part per 1000), the neodymium emission is quite intense even for exciting wavelengths which are absorbed only by Mn^{2+}. At room temperature the neodymium emission is considerably stronger than the manganese emission, which suggests that there is an efficient transfer of excitation energy from Mn^{2+} to Nd^{3+}. This communication describes the emission spectrum of the doped crystals and the temperature dependence of the energy transfer.

The host material, $CsMnBr_3$, is one of a number of AMX_3 halides which adopt linear-chain structures closely related to that of $CsNiCl_3$.[1] The $CsNiCl_3$ structure can be described as an array of parallel linear chains of MX_6^{4-} octahedra sharing opposite faces. The linear chains are anionic and have the stoichiometry $[MX_3^-]_n$. The univalent cations occupy positions between chains and balance the anionic charge. Since the intrachain separation between adjacent divalent metal ions is significantly shorter than the interchain separation, crystals of this type have a distinctly one-dimensional character. The magnetic properties of a number of AMX_3 salts have been extensively investigated.[2,3] The manganese salt $(CH_3)_4NMnCl_3$ (TMMC) has attracted particular attention since it behaves as a nearly perfect one-dimensional antiferromagnet. Recently, it has been shown that electronic excitation energy can rapidly migrate along the $[\mathrm{MnCl}_3^-]_n$ chains in TMMC. Yamamoto, McClure, Marzzacco, and Waldman concluded that the room-temperature hopping rate for the manganese excitation in TMMC is quite fast, approaching that observed in organic crystals.[4] Their work also indicates that the excitation energy may be trapped by metal ion impurities which have been introduced into the anionic chains; however, no emissions from the impurity ions were detected.

The spectroscopic and magnetic properties of CsMnBr_3 closely resemble those of $(\mathrm{CH}_3)_4\mathrm{NMnCl}_3$. This is consistent with the structural similarity of the two salts. Magnetic susceptibility and neutron scattering studies show CsMnBr_3 to be a quasi-one-dimensional antiferromagnet.[5,6] The susceptibility passes through a maximum at approximately 90 K. There is a three-dimensional ordering at 8.3 K. The intrachain exchange interaction is on the order of 7 cm^{-1} which is comparable to the 4.4-cm^{-1} value for TMMC.[7] The optical spectra of CsMnBr_3 and TMMC are similar in absorption energies and intensities.[8,9] It seems likely that the energy migration observed in TMMC is also a property of CsMnBr_3. In TMMC, the hopping rate of the manganese excitation decreases dramatically when the temperature is lowered to where the spins along the $[\mathrm{MnCl}_3^-]_n$ chains begin to couple strongly. Very little energy migration occurs below 50 K.[4] Therefore, it would be expected that the energy migration in CsMnBr_3 should diminish markedly below 90 K, the temperature of maximum magnetic susceptibility. Our experiments indicate that this is, in fact, the case.

EPR studies have shown that trivalent ions will enter the $[MX_3^-]_n$ chains when doped into crystals of the AMX_3 halides.[10-12] The major factor governing the incorporation of trivalent impurities into the anionic chains is the rather strict requirement for localized charge compensation. There are two primary modes for charge compensation in the linear-chain AMX_3 salts.[10,12] The first mode involves the association of two trivalent impurities with a divalent metal ion vacancy within a single $[MX_3^-]_n$ chain. The second mode results from the incorporation of a trivalent ion and a small monopositive ion into adjacent divalent ion sites of an $[MX_3^-]_n$ chain. The doped crystals used in this study were grown from melts of CsMnBr_3 containing Li^+ as well as Nd^{3+}. Thus, the principal Nd^{3+}-containing species present in the CsMnBr_3 crystals should be the Li^+-Nd^{3+} center. The Li^+-Nd^{3+} center is preferred in these studies, since Nd^{3+}-Nd^{3+} centers might undergo rapid nonradiative relaxation.

The manganese emission which arises from the lowest-energy ligand-field transition of the Mn^{2+} ion $({}^4T_1 \rightarrow {}^6A_1)$ consists of a broad featureless band centered at approximately 680 nm. In contrast to the manganese emission, the emission from neodymium is sharp and contains considerable structure. There are three major neodymium emission systems. These appear at 820, 890, and 1070 nm. The emission spectrum of a Nd^{3+} containing CsMnBr_3 crystal at several temperatures is shown in Fig. 1. The sensitivity of the photomultiplier tube (RCA 7102) used in this study drops significantly when the wavelength exceeds 1000 nm so that the neodymium emission at 1070 nm appears to be much less

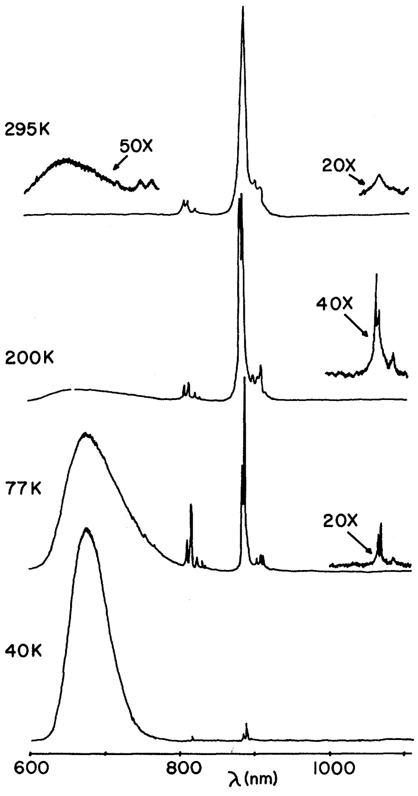

FIG. 1. Emission spectrum of a CsMnBr_3 crystal doped with Nd^{3+} and Li^+. A high-pressure xenon lamp with a CuSO_4-solution filter was used as an exciting source. The traces for the four different temperatures were recorded with approximately the same instrumental sensitivity. The raised portions of the traces were recorded with the sensitivity increased by the factors shown.

intense than those at 820 and 890 nm. The 890- and 1070-nm systems both originate from the $^4F_{3/2}$ excited state of the Nd^{3+} ion. The 890-nm system consists of transitions to the $^4I_{9/2}$ ground state, while the 1070-nm system results from transitions to the $^4I_{7/2}$ state which is approximately 2000 cm^{-1} above the ground state. The system at 820 nm most likely arises from transitions between the $^4F_{5/2}$ and $^2H_{9/2}$ excited states and the ground state. The relative intensities of different components within each of the emission systems show a noticeable temperature dependence. This suggests that thermal equilibration between some of the excited-state energy levels occurs before emission takes place. An excitation spectrum observed by monitoring the 890-nm emission at 200 K contains the features characteristic of the absorption spectrum of pure $CsMnBr_3$ but shows no evidence of direct neodymium absorption. It appears that the neodymium emission results primarily from energy transfer rather than direct absorption of the exciting radiation.

It is clear from Fig. 1 that the relative strengths of the neodymium and manganese emissions change drastically between room temperature and 40 K. Above 200 K the emission spectrum of the doped crystals is dominated by the systems from neodymium, while the broad manganese band accounts for almost all of the emission intensity below 40 K. This behavior is quite compatible with the observations of Yamamoto *et al.*[4] regarding energy migration in TMMC. It seems that $CsMnBr_3$ and TMMC must be at least qualitatively the same in this respect. At room temperature the hopping rate of the manganese excitation along the anionic chains is rapid. The excitation is trapped by the Nd^{3+} impurities, and the Mn^{2+} emission is nearly quenched. When the doped crystals are cooled the hopping rate decreases so that the manganese excitation is more localized. The manganese emission increases in intensity at the expense of the neodymium emission as the energy transfer becomes less efficient. Finally, at temperatures below 40 K, these appears to be very little energy transfer.

Several aspects of the energy migration and transfer in the Nd^{3+}-doped $CsMnBr_3$ crystals are significant. The present investigation and the previous EPR studies suggest that many trivalent ions including most of the rare earths can be introduced into crystals of the linear-chain AMX_3 salts (those salts which can be prepared from melts). It is quite likely that energy transfer between a variety of metal ions will occur in these materials. In $CsMnBr_3$, for example, any impurity which has a luminescing excited state at an energy less than that of the manganese $^4T_1$ state (~18 000 cm^{-1}) could, at least in principle, emit as a result of energy transfer. Since the transfer of energy can be monitored directly by observing the impurity ion emission, it should be possible to study the energy migration in these one-dimensional crystals in a very quantitative fashion. Above 100 K the Nd^{3+} emission from the doped $CsMnBr_3$ crystals is startlingly intense, orders of magnitude stronger than the emission from similarly doped $CsCdBr_3$ crystals. To a considerable extent this reflects the fact that the *f-f* transitions of Nd^{3+} are quite sharp and absorb over a small fraction of the spectral range while the Mn^{2+} ***d-d*** transitions are rather broad. The absorption spectrum of $CsMnBr_3$ covers a significant fraction of the spectral range between 600 and 300 nm. It seems that crystals such as $CsMnBr_3$ represent host lattices in which the excited states of rare-earth ions may be optically pumped with high spectral efficiency. Such materials may be useful in the construction of solid-state rare-earth lasers.

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[1] J. Goodyear and D. J. Kennedy, Acta Crystallogr., Sect. B 28, 1640 (1972).

[2] J. F. Ackerman, G. M. Cole, and S. L. Holt, Inorg. Chem. Acta 8, 323 (1974).

[3] L. J. de Jongh and A. R. Miedema, Adv. Phys. 23, 1 (1974).

[4] H. Yamamoto, D. S. McClure, C. Marzzacco, and M. Waldman, Chem. Phys. 22, 78 (1977).

[5] M. Eibschutz, R. C. Sherwood, F. S. L. Hsu, and D. E. Cox, in *Magnetism and Magnetic Materials—1972*, AIP Conference Proceedings No. 10, edited by C. D. Graham, Jr., and J. J. Rhyne (American Institute of Physics, New York, 1973), Pt. 1, p. 684.

[6] W. Breitling, W. Lehmann, R. Weber, N. Lehner, and V. Wagner, J. Magn. Magn. Mat. 6, 113 (1977).

[7] R. Dingle, M. E. Lines, and S. L. Holt, Phys. Rev. 187, 643 (1969).

[8] G. L. McPherson, H. S. Aldrich, and J. R. Chang, J. Chem. Phys. 60, 534 (1974).

[9] G. M. Cole, C. F. Putnik, and S. L. Holt, Inorg. Chem. 14, 2219 (1975).

[10] G. L. McPherson and L. M. Henling, Phys. Rev. B 16, 1889 (1977).

[11] L. M. Henling and G. L. McPherson, Phys. Rev. B 16, 4756 (1977).

[12] G. L. McPherson, W. Heung, and J. J. Barrazza, J. Am. Chem. Soc. 100, 469 (1978).