PHYSICAL REVIEW B VOLUME 3, NUMBER 9 1 MAY 1971

Optical Absorption Induced by Ca Impurities in MnF_2

D. D. Sell and S. E. Stokowski
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 22 December 1970)

We have measured the absorption spectrum of MnF_2 doped with 0.1% of Ca in the 18 100- to 18 400-cm^{-1} spectral region at 2 K. There is considerable weak structure in this region induced by the presence of the impurity. We concentrate upon two lines, Ca $E1$(I) at 18 122 cm^{-1} and Ca $E2$ (I) at 18 322 cm^{-1}, which we identify on the basis of their polarization as pure electronic transitions of Mn^{2+} ions perturbed by first-nearest-neighbor Ca^{2+} impurities. These two lines appear in π and σ, but not α polarization. Thus, the lines have both electric and magnetic dipole character and are consistent with a C_2 site symmetry for the absorbing ion. Stress results for the impurity transitions for [001]- and [110]-directed uniaxial stress are presented. It is found that the stress behavior of Ca $E1$(I) and Ca$E2$(I) is closely related to that of the intrinsic excitons $E1$ and $E2$, respectively.

I. INTRODUCTION

The lowest-energy optical transition of MnF_2 ($^6A_{1g} \longleftrightarrow {}^4T_{1g}$) has been studied in considerable detail in both absorption and fluorescence measurements. In pure crystals, the absorption spectrum consists of two magnetic dipole pure electronic transitions denoted as $E1$ and $E2$, followed by various electric dipole magnon and phonon sidebands at higher energy.[1] Fluorescence is seen from the lowest intrinsic exciton level $E1$ and its magnon sideband.[2]

There is a second type of transition induced by impurities with which we are concerned here. When impurities such as Ca, Mg, or Zn are introduced into the crystal, fluorescence occurs in the energy region below $E1$. In these cases, the impurities have no low-lying excited states of their own but act merely as a perturbation of the nearby Mn^{2+} excited states. The fluorescence corresponds to a transition from the lowest-energy perturbed $^4T_1$ state to the ground state.[3-6]

In this paper we are concerned with the absorption transitions to these same perturbed excited states. In absorption spectra we can study the higher-lying excited states that cannot be seen in the low-temperature fluorescence.

We have concentrated upon the case of calcium impurities. The spectral region of interest is shown in Fig. 1. In very pure crystals there is no structure for energies below $E1$. The two spectral lines of most interest are denoted as Ca$E1$(I) (18 122 cm^{-1}) and Ca$E2$(I) (18 322 cm^{-1}). The notation indicates, as we show below, that these are the $E1$ and $E2$ exciton lines perturbed by Ca impurities. The roman numeral in parentheses indicates that the fluorescing Mn ion is a first nearest neighbor of the Ca ion.

II. SITE SYMMETRY

The unitary site group for an unperturbed Mn ion in the antiferromagnetically ordered crystal is C_{2h}. Consequently, the pure electronic transitions must be purely magnetic dipole and must be polarized either parallel or perpendicular to the c axis (axis of magnetization). Following Loudon's notation,[7] "like" transitions (which transform as Γ_1^+ of C_{2h}) are polarized $\vec{H} \parallel c$, and "unlike" transitions (Γ_2^+) are polarized $\vec{H} \perp c$, where $\vec{H}$ is the magnetic vector of the light. $E1$ and $E2$ are like transitions; to date, unlike transitions have not been observed for the $^4T_{1g}$ manifold of MnF_2.

When an impurity ion is substituted at a Mn site in the lattice, the site symmetry of the neighboring Mn ions is reduced as indicated in Table I. Note that the perturbed sites do not have inversion symmetry; thus, electric dipole transitions are no longer forbidden. Experimental evidence indicates, however, that the admixture of odd parity into these primarily even-parity states is small, as witnessed by the fact that the electric dipole contribution to all of the observed impurity-induced electronic transitions is comparable to the magnetic dipole part.[3,4] The fluorescence studies[3-6] indicate that

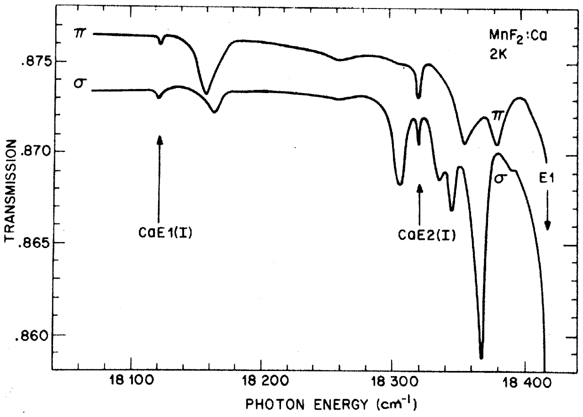

FIG. 1. Transmission at 2 K of a 1-cm path of MnF_2 doped with 0.1% Ca for σ and π polarization.

at least the first three nearest neighbors of a Mn ion can cause perturbed transitions. These three cases are considered in Table I.[4]

The two first nearest neighbors (referred to hereafter as first NN) are along the c axis. A first NN reduces the site symmetry to C_2.

For a body-centered ion, the eight second NN are at the corners of the unit cell. A second-NN impurity reduces the unitary site group to C_1, which yields no polarization information. However, we can make a reasonable "approximate" symmetry argument which should apply for weak perturbations such as we have here. If we consider only the symmetry of the electronic charge density (and ignore for the present the magnetic-moment density and time-reversal symmetry), the site symmetry becomes C_s', where the prime indicates that the mirror plane is one of the two (110) planes which contain the c axis. For C_s' symmetry, we obtain the results shown in Table I. The magnetic dipole transitions denoted by M' are not allowed in the unperturbed case. Thus, for relatively weak perturbations, we might expect them to be small compared with the M transitions which are allowed in the unperturbed crystal.

There are four third NN which lie in the plane normal to the c axis. In this case, the unitary site group is C_s with the reflection plane perpendicular to the c axis.

It can be seen from Table I that the polarization patterns tend to be quite distinctive. Thus, polarization data can generally be used (both for absorption and fluorescence) to determine the neighbor type and symmetry (like or unlike) of the unperturbed transition. An important exception to this rule is that the polarizations for the second-NN and third-NN like transitions are different only if M' is observed.

It should be noted that the polarization behavior of the first-, second-, and third-neighbor perturbed like transitions observed in fluorescence[3] are consistent with the results in Table I.

TABLE I. Site symmetry and polarization selection rules for perturbed like and unlike transitions of the Mn^{2+} ion. Types 1, 2, and 3 indicate that the perturbing impurity ion is at a first-, second-, or third-NN cation site to the Mn ion. Electric and magnetic dipole transitions are denoted by E and M, respectively. Polarizations are defined as follows: $\sigma(\vec{E}\perp c,\ \vec{H}\parallel c)$, $\pi(\vec{E}\parallel c,\ \vec{H}\perp c)$, and $\alpha(\vec{E}\perp c,\ \vec{H}\perp c)$.

Neighbor type	Site symmetry	Like transitions π	Like transitions σ	Like transitions α	Unlike transitions π	Unlike transitions σ	Unlike transitions α
Unperturbed	C_{2h}	···	M	···	M	···	M
1	C_2	E	M	···	M	E	E,M
2	$C_1\rightarrow C_s'$	M'	E,M	E,M'	E,M	E,M'	E,M
3	C_s	···	E,M	E	E,M	···	M

III. EXPERIMENTAL DETAILS

A sensitive double-beam spectrophotometer was used which allowed us to study lines with peak changes in transmission as small as 2×10^{-4} for a resolution of 0.5 Å with reasonable integration time constants (≤ 4 sec).[8] High sensitivity such as this (which is limited by the shot noise in the photomultiplier) is exceedingly difficult to obtain with a conventional single-beam apparatus. In our system, the sample is immersed in pumped liquid helium. One optical beam traverses the sample; the other beam also passes through the optical windows of the Dewar but passes beside the sample. The stress apparatus is similar to the apparatus used previously for modulated piezoreflectance measurements.[9] Here we use the same pneumatic-piston approach to apply dc stress to a sample mounted between copper or Teflon end pads (no Epoxy used) and immersed in pumped liquid helium. The samples used in the pressure experiments were either $1\times4\times5$ or $1\times5\times5$ mm.

Data were taken on samples from a boule of MnF_2 doped with 0.1 wt% of Ca grown by R. S. Feigelson of Stanford University which we obtained through the courtesy of J. F. Holzrichter. Both the integrated absorption strength and the broadening increase with the doping level. The 0.1% doping provides a reasonable compromise between signal strength and broadening (full width at half-maximum linewidth of approximately 4 cm^{-1} for $E1$).

IV. RESULTS

Figure 1 illustrates polarized data at 2 K for a 1-cm transmission path for photon energies somewhat smaller than the $E1$ intrinsic exciton (18419 cm^{-1}).[10] The α-polarized spectrum (not shown) is identical with the σ-polarized spectrum except for the lines Ca $E1$(I) and Ca $E2$(I), which are absent from the α spectrum. This indicates that all the structure is electric dipole except these two lines which have mixed electric and magnetic dipole character. From Table I we can see that this polarization behavior unambiguously identifies Ca $E1$(I) and Ca $E2$(I) as first-NN like (Γ_1^+) transitions.

The remainder of the structure presumably consists of various magnon and phonon sidebands of these transitions (or of other electronic transitions not seen). The combined effects of exciton-magnon interactions and local magnon modes make it very difficult to obtain good theoretical estimates for the sideband line shapes. Consequently, we shall not attempt to give a detailed analysis for these lines.

The lower-energy line Ca $E1$(I) has been studied in fluorescence. Its identity as a perturbed $E1$ exciton has been established by its polarization behavior[3] (i.e., its absence in α polarization) and by its stress behavior[4] which is the same as that of $E1$ measured by Dietz *et al.*[11]

We have also studied the absorption spectrum as a function of uniaxial stress along the [001] and [110] directions for stress levels to approximately 1000 kg/cm^2. Our results agree with the fluorescence results for Ca $E1$(I). In addition, we find that the structure near 18 160 cm^{-1} as well as the two π-polarized peaks at 18 356 and 18 380 cm^{-1}, shift with Ca $E1$(I). We also obtain the new information that the line Ca $E2$(I) shifts and splits with [001] and [110] stress as the intrinsic exciton $E2$. All the structure in σ polarization from 18 300 to 18 380 cm^{-1} has the same stress behavior as Ca $E2$(I). It is interesting that the band at 18 307 cm^{-1} has the same stress behavior as Ca $E2$(I) even though it appears at an energy below Ca $E2$(I). The nature of this band is not understood. If it were a "hot" band in which a phonon or magnon is absorbed, it could not be seen at 2 K.

None of the anticrossing behavior seen for $E1$ and $E2$ for [110] stress[11] is seen here. This is expected, since the two transitions in the unstressed perturbed system are separated by approximately 200 cm^{-1} and compressive stress tends to increase this energy separation.

It is interesting and somewhat surprising that Ca $E1$(I) and Ca $E2$(I) retain such a close identity to $E1$ and $E2$. The energies of the perturbed lines can be accounted for in terms of the two-substate model of Dietz *et al.*[11] for a very large compressive stress along [001] combined with a compressive hydrostatic stress. This tends to support an intuitive view, since the Ca ion is larger than the Mn ion.

These two lines show no evidence of an interaction with the other ten states of the $^4T_1$ manifold. This is in accord with the pseudo-Jahn-Teller effect for this state discussed by Meltzer and Lohr.[12]

Line Ca $E1$(I) has a peak strength in transmission of approximately 4×10^{-4} in π and 2×10^{-4} in σ indicating that the electric dipole transition strength is approximately twice that of the magnetic dipole transition. These relative intensities agree with the fluorescence data in Fig. 3(b) of Ref. 3. Furthermore, the magnetic dipole strength is approximately 10^{-3} of $E1$ which is consistent with a 0.1% impurity concentration.

On the other hand, the peak strength in transmission of Ca $E2$(I) is approximately 20×10^{-4} in π and 15×10^{-4} in σ. The simple two-substate model predicts equal intensities for Ca $E1$(I) and Ca $E2$(I). A possible explanation for this apparent discrepancy is that the model assumes that both states have the same vibrational overlap integral (Dietz *et al.*[5] estimate an overlap integral of 0.1). This may not be true even for the unperturbed excited states (the model gives only qualitative agreement with experimental intensities). Furthermore, the overlap for the perturbed states could differ from that for the intrinsic states.

For Ca impurities we observe only the first-NN perturbed transitions. This is in contrast to the fluorescence results for Zn and Mg impurities which exhibit only second- and third-neighbor perturbed transitions. The reasons for this difference are not well understood. It appears to be related to the fact that the Mn^{2+} ion is smaller than the Ca^{2+} ion, but larger than Zn^{2+} or Mg^{2+}. Presumably for Ca the second- and third-neighbor transitions fall at energies above $E1$. We do observe small differences between the Ca^{2+}-doped and pure-crystal spectra above $E1$. We have not attempted to study this region in detail, however, because the relatively strong intrinsic structure makes it difficult to study the weak impurity-induced effects. Conceivably, impurity-induced absorption results for Zn^{2+} or Mg^{2+} might clarify the situation.

ACKNOWLEDGMENTS

We gratefully acknowledge discussions with R. E. Dietz and assistance with sample preparation by A. J. Williams. We also thank R. S. Feigelson and J. F. Holzrichter for the crystals used in this study.

---

[1] D. D. Sell, R. L. Greene, and R. M. White, Phys. Rev. 158, 489 (1967).

[2] R. E. Dietz, A. E. Meixner, H. J. Guggenheim, and A. Misetich, Phys. Rev. Letters 21, 1067 (1968); J. Luminescence 1, 279 (1970).

[3] R. L. Greene, D. D. Sell, R. S. Feigelson, G. F. Imbusch, and H. J. Guggenheim, Phys. Rev. 171, 600 (1968).

[4] R. L. Greene, Ph.D. thesis (Stanford University, 1967) (unpublished).

[5] R. E. Dietz and A. Misetich, *Localized Excitations in Solids* (Plenum, New York, 1968), p. 366.

[6] R. E. Dietz and A. Misetich, Ref. 5, p. 379.

[7] R. Loudon, Advan. Phys. 17, 243 (1968).

[8] D. D. Sell, Appl. Opt. 9, 1926 (1970).

[9] D. D. Sell and E. O. Kane, Phys. Rev. 185, 1103 (1969).

[10] The apparent presence of $E1$ in π polarization results from a slight misalignment of the polarizer.

[11] R. E. Dietz, A. Misetich, and H. J. Guggenheim, Phys. Rev. Letters 16, 841 (1966).

[12] R. S. Meltzer and L. L. Lohr, J. Chem. Phys. 49, 541 (1968).