PHYSICAL REVIEW B VOLUME 18, NUMBER 10 15 NOVEMBER, 1978

# Shift and broadening of optical transitions in $MnF_2$:Zn

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(Received 6 March 1978)

The perburation on the optical properties of $MnF_2$, caused by the presence of small amounts of $Zn^{2+}$ ions substituted for $Mn^{2+}$ ions, is studied for Zn concentrations up to 1 at.%. In nominally pure $MnF_2$ pure electronic sharp-line and magnon sideband transitions involving the $^6A_{1g}$ ground state and the $^4T_{1g}$ excited state of Mn are observed in absorption and luminescence. These transitions shift to lower energies and broaden as the Zn concentration is increased. The broadening and shift are explained on the basis of the inhomogeneous strains introduced into the lattice by the Zn impurities and a simple strain theory of line broadening applied to $MnF_2$ yields values for the broadening which are close to the observed values.

## I. INTRODUCTION

The presence of some $Zn^{2+}$ ions, substituted randomly for $Mn^{2+}$ ions in $MnF_2$, upsets the long-range magnetic order of the Mn system, leading to a reduction in the energies of the spin-wave modes.[1] Since the magnon sidebands accompanying the sharp pure electronic optical transitions in $MnF_2$ reflect the distribution in energy of the spin-wave modes, one might hope to see the changes in the spin-wave spectrum by studying the sidebands in crystals of varying Zn concentrations. Attempts to carry out such optical experiments fail, however, because the pure electronic transitions also broaden considerably with increasing Zn concentration. We have measured this shift and broadening as the Zn concentration is raised from zero to approximately 1%, and we show that these effects can be attributed to inhomogeneous strains caused by the Zn impurities.

## II. EXPERIMENTAL DETAILS

Single crystals of $MnF_2$ of good optical quality, with seven different Zn concentrations in the region 0.1%–2%, were used in this study. A nominally pure $MnF_2$ sample was also studied that had a Zn concentration in the region of parts per million. The crystals were oriented by x-ray methods and polished in the required configurations for polarization studies. The Zn concentrations were measured by the technique of x-ray fluorescence, using the $K\alpha$ line of Zn. Even though the absolute concentrations can be determined to within a factor of 2 only by this technique, the relative concentrations can be determined to within about 5%. Tungsten light sources were used to measure the optical absorption, and a 200-W mercury arc lamp was used to excite fluorescence. The light was dispersed by a 1-m spectrograph and photoelectrically recorded. The overall resolution was 0.5 $cm^{-1}$. The samples were maintained at 1.7 K throughout by immersion in a bath of superfluid helium.

## III. ABSORPTION AND LUMINESCENCE IN $MnF_2$:Zn

$MnF_2$ has a rutile structure in which the Mn ions are arranged in a body-centered-tetragonal lattice. The lattice is composed of two interpenetrating identical sublattices at right angles to each other. Each Mn ion has two first- and four third-nearest neighbors on the same sublattice and eight second-nearest neighbors on the opposite sublattice. The site symmetry of $Mn^{2+}$ is $D_{2h}$. Below the Néel temperature of 67 K, the spins of the Mn ions align themselves antiferromagnetically along the principal axis such that the spins on the two sublattices are antiparallel. The optical properties of $MnF_2$, both nominally pure and doped with various cation impurities, have been studied extensively.[2-4] Our attention is centered on the transitions between the $^6A_{1g}$ ground state and the lowest excited $^4T_{1g}$ state. In absorption, these transitions consist of a zero-phonon part comprised of two sharp $\sigma$-polarized lines at 5429 and 5424 Å, which correspond to absorption from the lowest level of the ground state to the $E1$ and $E2$ exciton levels of $^4T_{1g}$, respectively. These lines are also denoted as $E1$ and $E2$. In addition, $\sigma$- and $\pi$-polarized magnon sidebands of these lines are observed as is a broad phonon sideband extending to about 4500 Å. The spectrum of $E1$ and $E2$ and their associated magnon sidebands is shown in Fig. 1 for nominally pure and various Zn-doped samples. The broadening of the lines and their shift towards lower energy with increasing Zn

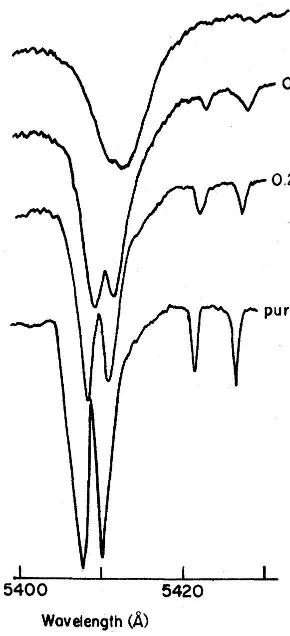

FIG. 1. $^6A_{1g}\rightarrow{}^4T_{1g}$ absorption spectra of $Mn^{2+}$ in $MnF_2$: $Zn^{2+}$ at four different Zn concentrations. *E*1 and *E*2 are the pure electronic transitions and $\sigma$1 and $\sigma$2 are the magnon sidebands of *E*1 and *E*2, respectively.

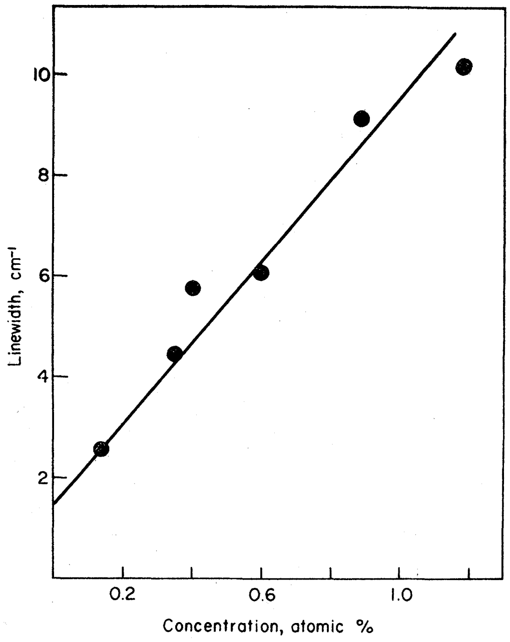

FIG. 2. Width of the *E*1 absorption line of $Mn^{2+}$ as a function of Zn concentration in $MnF_2$.

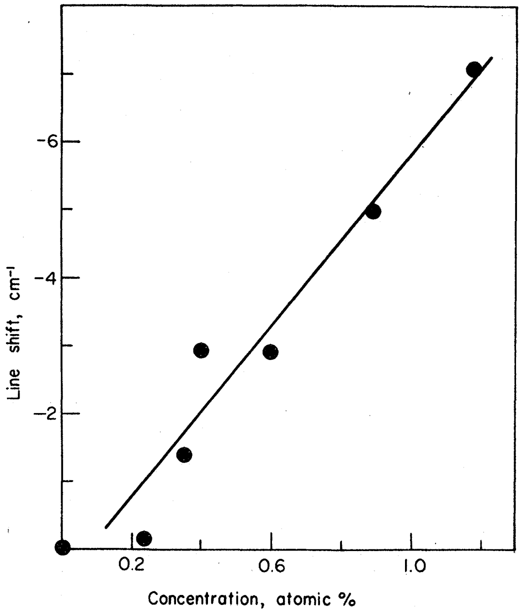

FIG. 3. Position of the *E*1 absorption line of $Mn^{2+}$ as a function of Zn concentration. The position is expressed in terms of the shift of the line from the position of *E*1 in a pure sample.

concentration is apparent. The linewidth and line shift for all of the samples are plotted in Figs. 2 and 3, respectively, as a function of Zn concentration. A linear dependence on concentration is seen for both the linewidth and line shift.

As *E*1 is the lowest excited state of Mn, luminescence is expected to occur from this state to the ground state. In a very pure sample a small amount of intrinsic luminescence has been observed at the *E*1 wavelength,[5] but most of the sharp line luminescence occurs at higher wavelengths. By intentionally doping $MnF_2$ crystals with small amounts of Zn, Mg, and Ca ions, the luminescence lines have been identified as originating from Mn ions which are near neighbors to these impurities,[4] and these Mn ions are populated by energy transfer from the regular Mn ions. In our Zn-doped samples, the luminescence lines originate from Mn ions which are near neighbors to Zn ions. These lines also broaden and shift with increasing Zn concentration in a manner similar to that of *E*1 and *E*2 in absorption. This is seen in Fig. 4. The line marked as Zn(3nn) is a zero-magnon line originating from Mn ions which are third-nearest neighbors to Zn ions, while that marked Zn(2nn) originates on Mn ions which are second-nearest neighbors to Zn ions. The $^4T_{1g}$ levels of the second- and third-nearest neighbor Mn ions from which these transitions

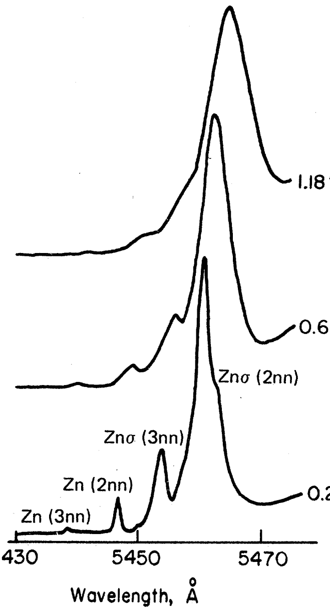

FIG. 4. ${}^4T_{1g}\rightarrow{}^6A_{1g}$ luminescence spectra of $Mn^{2+}$ in $MnF_2$: Zn for different concentrations of Zn. The Zn (3nn) and Zn (2nn) lines originate on Mn ions, which are third- and second-nearest neighbors to $Zn^{2+}$ ions, respectively. Znσ (3nn) and Znσ(2nn) are the magnon sidebands of Zn (3nn) and Zn (2nn), respectively.

occur are both lower in energy than the $E1$ exciton band and are depressed by 66 and 36 $cm^{-1}$, respectively, in samples containing only trace amounts of Zn. No sharp line luminescence is seen from Mn ions which are first-nearest neighbors to Zn ions. Nevertheless, from broadband luminescence in Zn-doped $MnF_2$ we see evidence of a deep Mn trap at about 300 $cm^{-1}$ below the $E1$ level, which is presumably due to such first-nearest-neighbor Mn ions. It is interesting to note that in Ca-doped $MnF_2$ crystals a sharp line originating on Mn ions which are first-nearest neighbors to Ca ions has been observed at about 300 $cm^{-1}$ below the $E1$ level.[4] All of this suggests that around each Zn ion there is a strain field which lowers the ${}^4T_1$ levels of nearby Mn ions. The nearer the Mn ion is to the impurity, the lower is the ${}^4T_1$ level. We attribute the observed shift and broadening of the absorption and luminescence transitions to the inhomogeneous strains brought about by the random distribution of Zn ions in the $MnF_2$ lattice.

## IV. STRAIN ANALYSIS

Stoneham[6] has developed a theory for the shift and broadening of transitions between nondegenerate electronic levels in solids caused by random strains in the solid. We shall use this theory to analyze the shift and broadening of the pure electronic $E1$ absorption transition in Zn-doped $MnF_2$. If one assumes that the lattice is an isotropic homogeneous continuum and that the defects are distributed at random throughout the lattice, then Stoneham shows that the lines broaden and shift linearly with the concentration of defects. The size of the shift and broadening depends on the sensitivity to strain of the optical transitions as well as on the extent of the strain caused by each type of defect.

The strain due to a point defect a distance $\vec{r}(x_1, x_2, x_3)$ away is assumed to be given by

$$\epsilon_{ij}=(A/r^3)(\delta_{ij}-3x_ix_j/r^2), \qquad (1)$$

where $A$ is a constant for the particular defect-in our case, the $Zn^{2+}$ ion occuring substitutionally for a $Mn^{2+}$ ion.

The line shift due to strains $\epsilon_{ij}$ is written

$$\Delta E=\sum_{i,j}a_{ij}\epsilon_{ij}, \qquad (2)$$

where the $a_{ij}$ components measure the sensitivity of the optical transition to strain. The line shift caused by a Zn ion a distance $\vec{r}$ away is, then,

$$\Delta E=\frac{A}{r^3}\sum_{i,j}a_{ij}\left(\delta_{ij}-\frac{3x_ix_j}{r^2}\right)=\frac{A}{r^3}\psi. \qquad (3)$$

The random distribution of such Zn ions leads, in the continuum approximation, to a Lorentzian line shape whose width is given by

$$\Gamma_L=\tfrac{1}{3}\pi\rho|A|\int|\psi|\,d\Omega, \qquad (4)$$

where $d\Omega=\sin\theta\, d\theta\, d\phi$, and $\rho$ is the density of Zn ions. The integral in Eq. 4 is difficult to evaluate, but Davies[7] showed that to a good approximation one can write

$$\int|\psi|\,d\Omega\simeq 3\left(\sum_{\alpha,\beta}c_{\alpha\beta}a_\alpha a_\beta\right)^{1/2}, \qquad (5)$$

where each subscript $\alpha$ or $\beta$ refers to the two-integers label $ij$, and the values of the $c_{\alpha\beta}$ coefficients are tabulated by Davies. We then have a formula for the strain broadening,

$$\Gamma\simeq\pi\rho|A|\left(\sum_{\alpha,\beta}c_{\alpha\beta}a_\alpha a_\beta\right)^{1/2}. \qquad (6)$$

To evaluate this formula we need to know the values of $\rho$, $A$, and each of the $a_{ij}$ components.

If the elastic constants of $MnF_2$ are known, the values of the $a_{ij}$ components can be found by making a series of static strain measurements to determine the changes in line position under various applied stresses. Uniaxial strain measurements have been made by Dietz *et al.*,[8] and from the unpublished work of McSkimin, quoted by Davis *et al.*,[9] we know that the Young's modulus for $MnF_2$ is approximately $10^{12}$ dyn $cm^{-2}$. These data, however, are insufficient to determine all the $a_{ij}$ components; they yield only an average value: $a_{ij} = a = -6\times 10^3$ $cm^{-1}$.

To obtain $A$ we apply Eqs. (1) and (2) to the case where the Zn ion is in a third-nearest-neighbor cation site—a distance $r = 4.87$ Å in a direction perpendicular to the $c$ axis from the Mn ion in question. The sharp luminescence line originating on this Mn ion [line Zn(3 nn) in Fig. 4] is shifted by $\Delta E = -36$ $cm^{-1}$ from the $E1$ line. We will assume that this shift is correctly calculated by the application of Eqs. (1) and (2), and we get

$$-36\ \text{cm}^{-1} = -2a_{xx}A/r^3\ ,$$

giving $A = 3.5\times 10^{-25}$, where the line shift is measured in $cm^{-1}$ and all other quantities are measured in cgs units.

For a 1% atomic concentration of Zn we have $\rho = 10^{20}$ $cm^{-3}$, and using the values of $A$ and $a_{ij}$, we estimate a linewidth from Eq. (6) of 6.5 $cm^{-1}$, which is very close to the experimental value of 9.5 $cm^{-1}$.

In view of our limited knowledge of the strain parameters, we can also adopt a simpler isotropic continuum model which assumes that the optical transition on a Mn ion which is a distance $r$ away from a defect (Zn ion) is shifted by an amount $\Delta E$, where

$$\Delta E = B/r^3\ , \tag{7}$$

and that the line shifts of a transition on a particular Mn ion due to a number of nearby Zn ions add linearly. In this case, Stoneham's formula for the linewidth becomes

$$\Gamma = (4\pi^2/3)\rho\,|B|\ . \tag{8}$$

We can obtain $B$ from the $-36$-$cm^{-1}$ line shift on the Mn ion with a Zn ion as a third-nearest cation neighbor ($r = 4.87$ Å). This gives $B = -4.16\times 10^{-21}$ $cm^{-4}$. Consequently, for a 1% Zn concentration we calculate a linewidth of 5.5 $cm^{-1}$.

In addition to the above calculations, which are based on an isotropic continuum approximation, we estimated the shift and broadening in a 1% Zn sample by plotting an approximate histogram of the number of actual Mn-Zn centers which can occur in $MnF_2$ against the expected line shift of each center, as calculated using Eq. (7) and the above value of $B$. This predicts a broadening of approximately 7 $cm^{-1}$, similar to that calculated above, and the histogram shows that the center of gravity of the broadband line should shift to lower energy by about 9 $cm^{-1}$, again in approximate agreement with experiment.

## V. CONCLUSION

In view of our limited knowledge of the strain parameters for the $MnF_2$ system, the calculations of the broadening and shift due to the Zn-induced strains are necessarily approximate. Nevertheless, there is sufficient agreement between the calculated and observed values to confirm that the strains caused by the random distribution of Zn ions in the $MnF_2$ lattice can explain the shift and broadening in the optical transitions in $MnF_2$:Zn.

## ACKNOWLEDGMENTS

We wish to thank H. Guggenheim for some of the crystals which were used in this study. We are also indebted to D. L. Huber for many invaluable discussions. Work at the University of Wisconsin was supported by the NSF under Grant No. DMR76-21574 and at University College Galway by the Irish National Science Council under Grant No. URG/18/77.

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