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Shift and broadening of electronic transitions in a dilute antiferromagnet: $Fe_{1-x}Zn_xF_2$

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The effects of dilution on the crystalline field, the exchange field, and the Néel temperature have been studied for the dilute antiferromagnet $Fe_{1-x}Zn_xF_2$ in the range of $0 \leq x \leq 0.75$. Excitations within the ${}^5T_{2g}$ manifold of Fe^{2+} ions have been measured by Raman scattering, and the one-magnon sideband transition in the 21 500-cm^{-1} region was studied by optical absorption. Both transitions shift and broaden as the zinc concentration is increased. The behavior of the main features of the spectra are interpreted in terms of a molecular-field model. From the Raman measurements a linear change of the magnetic anisotropy with zinc dilution was deduced, while the shift of the one-magnon sideband indicates a linear variation of the exchange field and the Néel temperature with x. The low-temperature linewidths are interpreted as originating from the random distribution of Fe^{2+} environments and strains induced by the zinc ions. The results confirm many theoretical assumptions of previous papers.

I. INTRODUCTION

In recent years, the behavior of magnetic and electronic properties of disordered magnetic insulators has attracted considerable attention.[1] In particular the rutile compounds of Mn^{2+} have been playing an important role in the study of disordered magnetic materials since they approximate well with simple "model systems."[1] Interesting observations based on a large variety of techniques such as neutron scattering,[2] NMR,[3] Raman scattering,[4] birefringence,[5] far-infrared,[6] and microwave absorption[7] have been reported.

Another class of important materials includes the Fe^{2+}-doped crystals. These systems differ very much from the manganese compounds by their strong magnetic anisotropy field which may assume values comparable with the magnitude of the exchange field. Although theoretical treatments for Hamiltonians appropriate to these systems have become increasingly sophisticated,[8–10] experiments on three-dimensional Fe^{2+} "model systems" are still very scarce.[11–15] For this reason we have chosen to study the diluted antiferromagnet $Fe_{1-x}Zn_xF_2$. This is a particularly attractive system in which to make a detailed study of the magnetic and electronic properties in the sense that it exemplifies a class of three-dimensional antiferromagnetic alloys of high anisotropy.

$Fe_{1-x}Zn_xF_2$ has the tetragonal rutile structure D_{4h}^{14} in which the cations are arranged on a body-centered tetragonal lattice. The point symmetry at the positions of the Fe^{2+} ions is D_{2h}. Below the Néel temperature these compounds become antiferromagnetically ordered with spins of the two sublattices aligned along the c axis. Their magnetic properties are mainly determined by the influence of the crystal field on the electronic ground state, which becomes apparent in the single-ion-anisotropy of the Fe^{2+} ion. As in pure FeF_2 (Ref. 2) the crystal field in the $Fe_{1-x}Zn_xF_2$ should split the five orbital states of the Fe^{2+} into a lower ${}^5T_{2g}$ orbital triplet consisting of states with symmetry ${}^5A_{1g}$, ${}^5B_{1g}$, and ${}^5B_{2g}$ and an upper ${}^5E_g$ doublet consisting of two orbital states with ${}^5A_{1g}$ and ${}^5B_{3g}$ symmetry. The two groups of levels should be separated by about $\approx 10^4$ cm^{-1} as in pure FeF_2.[2]

In spite of the increased interest in magnetic alloys $Fe_{1-x}Zn_xF_2$ did not receive much attention in the past. To our knowledge Ref. 11 is the only experimental report on $Fe_{1-x}Zn_xF_2$ which appeared in the literature prior to the last two years. They report on Mössbauer experiments with crushed powders prepared from polycrystalline melts of FeF_2 and ZnF_2 with different compositions. A very interesting result of this experiment is the behavior of the Néel temperature $T_N(x)$ which does not vanish as the zinc concentration tends to the percolation limit. Only recently[8,10] this result was theoretically explained as due to the high magnetic anisotropy of this system.

The first report on crystalline $Fe_{1-x}Zn_xF_2$ appeared recently in the literature.[12] Antiferromagnetic resonance and magnon-pair excitations in this alloy were studied by light scattering as a function of the concentration x and the temperature. One of the results of this experiment is the fact that in the highly diluted samples the one-magnon frequency ($k \simeq 0$) does not vanish at the Néel temperature. This phenomenon which may not be explained in the framework of previous theories[8–10] was interpreted as an indication of the existence of coupled clusters of magnetic ions and was described by a simple model which could predict the position of the Raman peaks as well as the line shapes.

Other optical studies on this system have appeared very recently in the literature.[13,14] In Ref. 13 preliminary results of the electronic Raman scattering for $Fe_{1-x}Zn_xF_2$ were reported as a function of temperature and dilution, while in Ref. 14 the measurements of the temperature derivative of the linear magnetic birefringence have been used to study the effects of dilution on the Néel temperature and the short-range order in these rutile systems.

The purpose of this article is to present results of further optical measurements on $Fe_{1-x}Zn_xF_2$. Both optical-absorption and light scattering techniques have been used to probe electronic transitions in this magnetic alloy. The shift and broadening of the optical transitions were then used to deduce the variation of the anisotropy and the exchange field as a function of the zinc concentration. Also deduced from the absorption data were the Néel temperature for each sample. The results are compared with the available theories and/or with previous experimental data obtained by other techniques.[11,14]

II. EXPERIMENTAL

The data presented here were obtained with crystals grown by N. Nigman of the University of California at Santa Barbara. Single crystals of $Fe_{1-x}Zn_xF_2$ of good optical quality with seven different zinc concentrations in the range of 5% to 75% were used in this study. The crystals were mounted in a cold-finger Dewar with temperature measured by a thermocouple embedded in the mounting bracket. The temperature of the samples could be varied from 10 to 300 K with regulation of 0.1 K.

The Raman measurements were made with the incident light propagating parallel to the c axis of the samples. An argon-ion laser of either 4880 or 5145 Å was used with power below 100 mW to avoid sample heating effects. The scattering plane was perpendicular to the c axis and the right-angle scattered light was analyzed using a double spectrometer, a low-noise photomultiplier, and dc current detection.

The absorption spectra were taken using a tungsten light source and a grating spectrograph with instrumental width of about 2 cm^{-1}.

III. RESULTS AND DISCUSSION

First is described the electronic Raman scattering experiment. In the measurements I investigated Raman transitions between electronic levels of the ground $^5T_{2g}$ multiplet of Fe^{2+} ions, their splitting, and linewidths.

Figure 1 shows a typical Raman spectrum for $Fe_{0.95}Zn_{0.05}F_2$, where the 4880-Å line of an argon laser was used as the exciting light. Similar to pure FeF_2,[16] the low-temperature spectrum shows an intense peak in the region of $\approx 10^3$ cm^{-1}

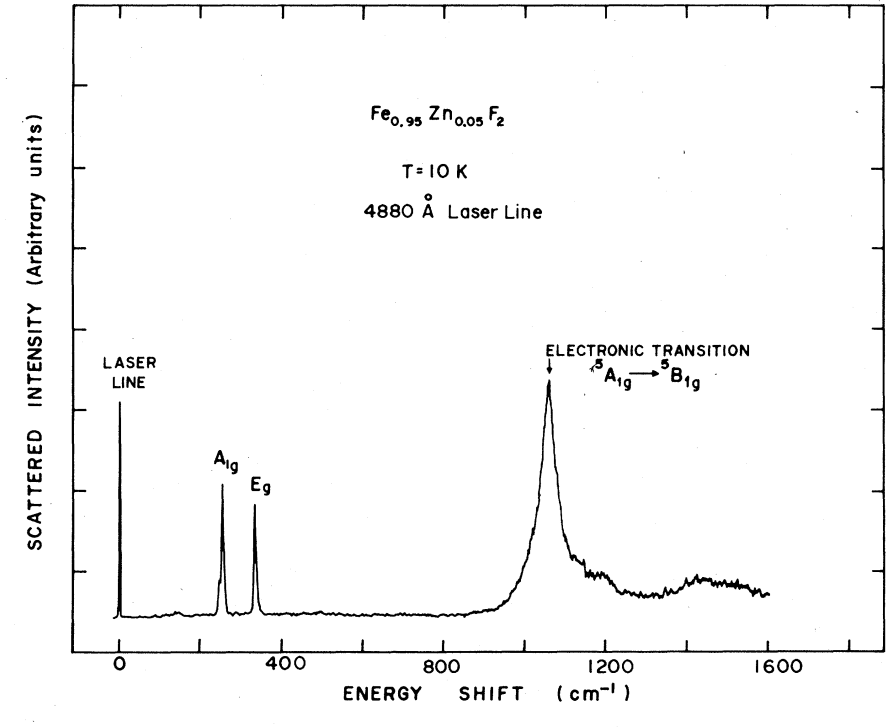

FIG. 1. Electronic Raman spectrum of $Fe_{0.95}Zn_{0.05}F_2$ at low temperature (10 K). The Rayleigh line is reduced by several orders of magnitude to be shown in the same spectrum.

which is associated to a Raman transition from the ground state $^5A_{1g}$ to an excited electronic state of $^5B_{1g}$ symmetry. The other peaks in the spectrum are the A_{1g} and E_g phonons located at ≈ 340 and ≈ 260 cm^{-1}, respectively. The region from ≈ 30 to ≈ 140 cm^{-1} inlcudes the one- and two-magnon scattering which were studied in a previous paper.[12] The low values of the magnon cross sections in comparison with the electronic Raman scattering makes it impossible to record both features with same sensitivity.

The behavior of the strong electronic Raman peak with sample temperature was studied for different dilutions. The measurements indicate that the peak does not shift from 10 K up to the Néel temperature, $T_N(x)$. However its intensity decreases when the temperature is increased although its linewidth does not change. Near T_N the peak disappears into a broad asymmetric background which can be observed even at room temperature. These features were observed for all crystals irrespective of concentration. In Fig. 2 is shown the dependence of the electronic Raman peak intensity and linewidth with the temperature for two studied samples. Note that for pure FeF_2 the linewidth remains constant for a large range of temperatures. However, for high temperatures $[T \approx T_N(x)]$, when the Raman line almost disappears into the asymmetric background, the linewidth becomes temperature dependent. For other samples studied the behavior is essentially the same. For $Fe_{0.95}Zn_{0.05}F_2$ the linewidth is temperature independent up to ≈ 40 K while for $Fe_{0.88}Zn_{0.12}F_2$ and $Fe_{0.72}Zn_{0.28}F_2$ the measurements show the same trend up to ≈ 30 K. The dependence of the integrated intensity upon the temperature is difficult to describe quantitatively because of the broad background. However, its behavior indicates that the scattering depends on an intermediate magnetically ordered state as suggested in the case of pure FeF_2.[16] It has also been observed that, different from that which should occur in nonmagnetic crystals[17] the scattering intensity decreases faster than linearly with x. These results may explain the nonappearance of the electronic transition for samples of MgF_2 and MnF_2 doped with Fe^{2+} impurities.[16]

Figure 3 shows the Raman shift $\Delta(x)$ corresponding to the transition $^5A_{1g} \rightarrow {}^5B_{1g}$ as a function of zinc concentration. The shift varies linearly with x and changes about 10% between $x=0$ and 0.75. This linear dependence was expected from the behavior observed for other electronic transitions in doped systems[18] and in the present case may be characterized by using an effective single-ion anisotropy Hamiltonian with axial symmetry.[2] This assumption allows one to analyze the anisotropy field $H_A(x)$ as a function of

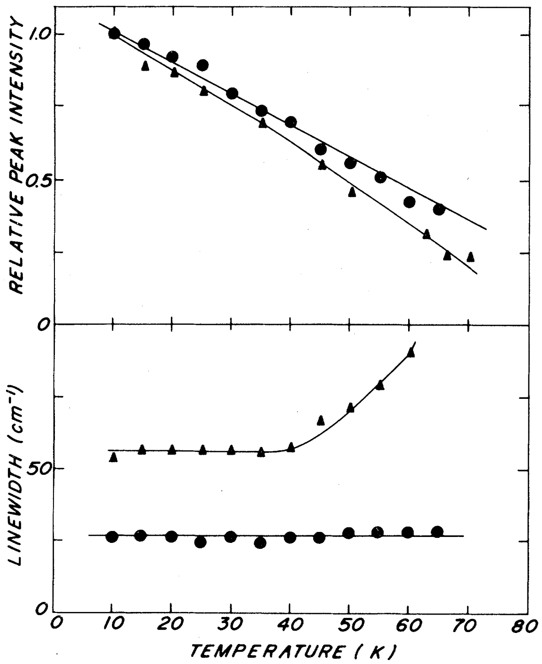

FIG. 2. Relative peak intensity and linewidth of the electronic Raman transition $^5A_{1g} \rightarrow {}^5B_{1g}$ as a function of temperature for two samples: $x=0$ (●) and 0.05 (Δ).

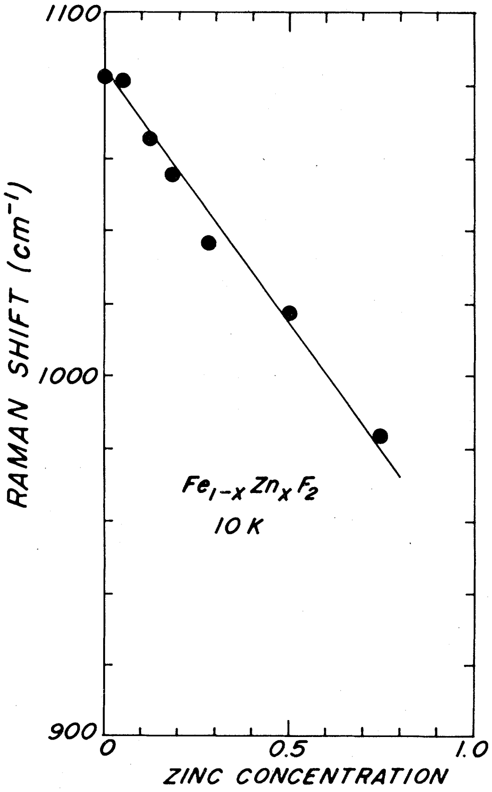

FIG. 3. Shift of the electronic Raman line as a function of zinc concentration. It is a direct measurement of the splitting between $^5A_{1g} \rightarrow {}^5B_{1g}$ levels.

the zinc dilution in an indirect way. The model for $H_A(x)$ can be built using some results of previous Mössbauer studies. In Ref. 11 it becomes clear that although the neighborhood of an iron ion depends on the dilution, the Fe^{2+} radial wave function and the local symmetry D_{2h} are essentially the same for all values of x. Accordingly, the spin-orbit parameter is supposed to be dilution independent and one may assume that all variation in $H_A(x)$ is due to changes in the crystalline field. A microscopic model for the single-ion anisotropy field is described in many textbooks.[19] In the present case we treat the system as an equivalent "two-level system" and obtain $H_A(x)=(2s-1)\lambda^2|\Delta(x)|^{-1}$. By using the Raman shift values $\Delta(x)$ for the transition ${}^5A_{1g}\rightarrow{}^5B_{1g}$ we obtain the ratio $H_A(x)/H_A(0)$ which is plotted in Fig. 4 showing an approximate straight-line behavior. This result confirms the assumptions previously done by Tahir-Kheli *et al.*[10] and Montarroyos *et al.*[12] to describe the Néel temperature and the magnon energies in these crystals. In both cases, a straight line was interpolated between values for the anisotropy field for pure FeF_2 and Fe^{2+}-doped ZnF_2, and the agreement with the experiment was quite reasonable. Note however that, although the Raman data allow one to deduce the behavior of $H_A(x)$, one cannot calculate its absolute value accurately due to the uncertainty in the λ value which is obtained fitting from Mössbauer data.[20] However, a numerical estimate using $\lambda\sim 85$ cm^{-1} is in reasonable agreement with the magnitude of previously published values,[21,22] $H_A(0)=19.5$ cm^{-1} and $H_A(1)=24.9$ cm^{-1}. Moreover, as has been pointed out previously[13] the Raman shift allows one to obtain the g factor which is given by $g(x)=2(1-\lambda|\Delta(x)|^{-1})$. For $x=0$ and $x\sim 1$ this formula gives results in the range of the reported values,[11] i.e., 2.25 ±0.05.

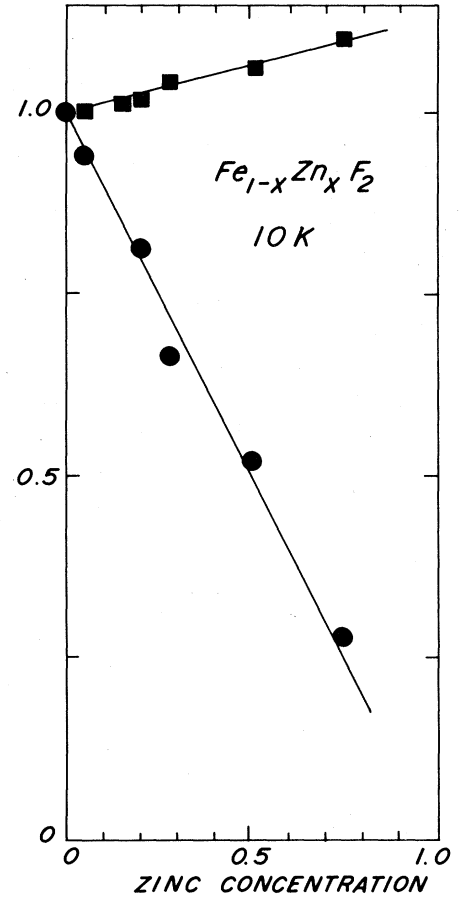

FIG. 4. Variation of the anisotropy field, $H_A(x)/H_A(0)$, (■) and the exchange field, $H_E(x)/H_E(0)$, (●) as a function of zinc concentration.

A comparison between Figs. 5 and 2 shows that the behavior of the linewidths as a function of zinc concentration at low temperatures indicates that this electronic line is inhomogeneously broadened, probably due to the combined effect of strains and clustering of magnetic ions. Both effects are known to be important in describing other electronic linewidths in disordered materials.[18,23–25] In the case of $Mn_{1-x}Zn_xF_2$ with small zinc concentrations, it was shown by applying Stoneham's formalism[18,23] that the shift and broadening of the optical transitions are due to inhomogeneous strains resulting from the random distribution of Zn ions in the MnF_2 lattice. This result suggests that also here the strain effect should be the important broadening mechanism in the limit where $x\rightarrow 0$. In order to apply Stoneham's theory,[23] we first consider the total linewidth to be a sum of the disorder inhomogeneous contribution $\Gamma_D(x)$ and a homogeneous part which is obtained from the measurement of pure FeF_2 ($\Gamma_H=28$ cm^{-1}). The order of magnitude for $\Gamma_D(x)$ in the limit of small x can be calculated in the same way as in Ref. 18. Assuming the same order of magnitude for the elastic constants

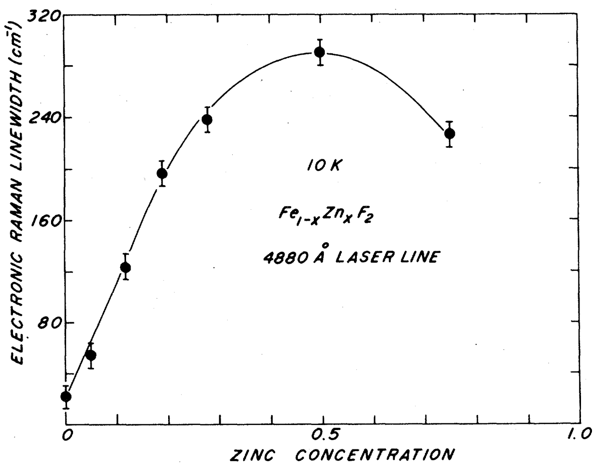

FIG. 5. Linewidth of the scattered electronic Raman line as a function of zinc dilution.

of FeF_2 as in MnF_2 at low temperature,[18,26] we estimate for $x=0.05$ the value $\Gamma_D(x)=30$ cm^{-1} which added to the homogeneous linewidth leads to a reasonable agreement with the experiment, $\Gamma_{\text{expt}}=55$ cm^{-1}. For large x the assumption of the lattice as an isotropic homogeneous continuum of Stoneham's theory fails due to the clustering of magnetic ions and thus cannot be applied. As an alternative approach one may consider the broadening theory developed by Dorman in Ref. 24. This theory which takes into account clustering effects has been successfully applied for transition metals[25] and rare-earth ions[24] in nonmagnetic hosts. In the present case the range of possible values for $\Delta(x)$ imposes a constraint on the maximum value for the disorder linewidth which should be of the order of ≈ 140 cm^{-1} leading to a total value of ~ 168 cm^{-1}. Obviously this value does not fit the large experimental linewidth (~ 290 cm^{-1}) for $x=0.50$ and from this analysis one may conclude the probable existence of other than the broadening mechanisms suggested above. Clearly further effort should be developed to clarify this point.

The information obtained in the Raman experiments could be reinforced and extended by measuring the absorption spectra associated with electronic transitions between Fe^{2+} levels and investigating its behavior as a function of temperature and dilution. In fact, the spectra of ordered antiferromagnets have been actively investigated in the past years and their major features are understood.[28] In particular the axial spectra of pure FeF_2 have been studied by different authors[27-30] and much attention has been focused on the 21 500-cm^{-1} region. It consists of an electronic magnetic-dipole transition at 21 504 cm^{-1} with associated one-magnon sideband at 21 568 cm^{-1} which is very strong and a weak two-magnon sideband absorption at 21 631 cm^{-1}. The same features were observed in our $Fe_{1-x}Zn_xF_2$ samples at wavelengths shifted from the corresponding ones at pure FeF_2 by energies which depend on the zinc concentration. Since the major interest here is to obtain information related to the magnetic structure we concentrate on the one-magnon sideband transition and study its behavior as a function of the temperature and dilution. These lines move as an effect of the temperature and their displacement from the position at 0 K as a function of T may provide information on the exchange field or the sublattice magnetization.[28] To understand this behavior we neglect the exciton dispersion, assume that the excitation stays on one ion and consider the excited ion as being in a large exchange magnetic field due to the neighbors. As the temperature is increased thermal disorder reduces the spin alignment and the exchange field acting upon the excited ion is reduced as well as the sublattice magnetization. As a consequence, the energy of the transition changes in the same way as the magnon energy. Using this simple model and assuming that at these temperatures most of the spin deviations are due to zone-boundary magnons the exchange field can be deduced.

The obtained results are plotted in Fig. 4 showing for $H_E(x)/H_E(0)$ a linear behavior with the zinc dilution. These results confirm the previous assumptions of Refs. 10 and 12. The straight line of Fig. 4 fits well the experimental points and extrapolates to zero when $x \rightarrow 1$. The assumption of zone-boundary (ZB) magnons participating in the transition has been used before[28] to determine the exchange parameters of FeF_2. Though the ZB magnons in FeF_2 have energies of ~ 77 cm^{-1} the value of 64 cm^{-1} deduced from the optical-absorption experiment is not surprising and does not affect too much the exchange field. This energy reduction has been observed in other antiferromagnetic insulators and might be due to exciton dispersion or magnon-exciton interactions[29] which were neglected.

From the same absorption measurements one can deduce the Néel temperature of the crystals. It can be done in the framework of the molecular-field approximation assuming that T_N corresponds to the

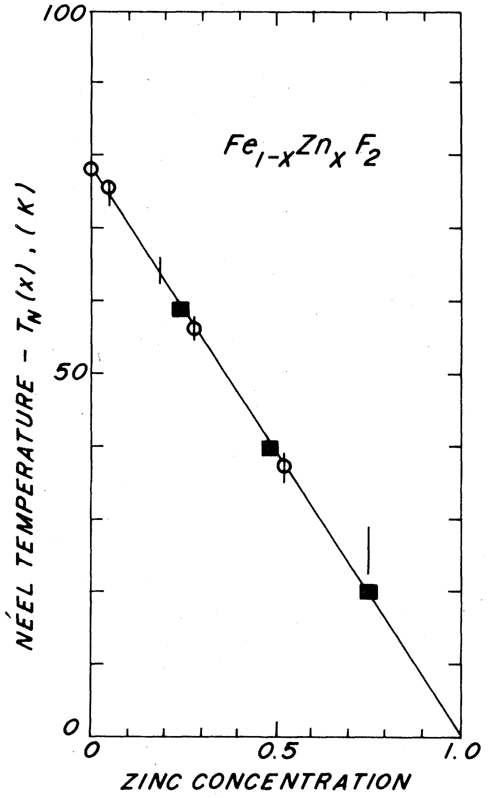

FIG. 6. Néel temperature vs the zinc concentration. The bar (|) refers to results obtained in the present work. Squares (■) and circles (○) are from Refs. 11 and 14, respectively.

temperature at which the exchange field vanishes, or equivalently, the temperature from which the absorption line stops shifting. The $T_N(x)$ values obtained in this way are plotted on Fig. 6. Also plotted on the figure are the results of Refs. 11 and 14. The agreement with the previous results is reasonable except for the larger concentrations ($x = 0.75$). The disagreement in this case can be understood considering that for large dilution it is expected that the simple molecular-field model fail due to the role played by the short-range-order effects which become very important in that limit.[14] Our result at $x = 0.75$ is larger than the Mössbauer result,[11] $T_N = 20$ K, and the birefringence measurement[31] which provides $T_N(x = 0.75) < 25$ K. The solid line connecting the points corresponds to $(d/dx)|T_N(x)| \approx 1$. This behavior agrees with a coherent-potential approximation calculation by Tahir-Kheli *et al.*[10] and results from the fact that the system is expected to become more Ising-like with dilution. Other phenomena such as increasing the short-range-order effect and reduction of the effective dimensionality of the magnetic systems near the percolation limit may also affect the results. Both have been the subject of recent investigations with two-dimensional systems,[32] but studies on three-dimensional alloys are not yet available.

In conclusion, we have shown that electronic Raman scattering as well as optical absorption are useful techniques to study the energy levels of Fe^{2+} ions in antiferromagnetic alloys. The results for exchange, anisotropy field, and $T_N(x)$ confirm many assumptions and results of previous papers.[8–14] In view of our limited knowledge of the strain parameters in $Fe_{1-x}Zn_xF_2$ the calculations of shift and broadening of the electronic transitions are necessarily approximate. The results in the limit of small zinc concentration are well understood but the large linewidth at $x = 0.50$ remains unexplained.

One question which was left open to future research is a more accurate microscopic description of the magnetic anisotropy in $Fe_{1-x}Zn_xF_2$. The behavior of other electronic states as well as the variation of the spin-orbit coupling due to covalency effects should be clarified for any further calculations.

Another extension of this work may be achieved by measuring the interterm Raman scattering from ${}^5T_{2g} \rightarrow {}^5E_g$ Frenkel excitons in $Fe_{1-x}Zn_xF_2$. This transition was previously studied for pure FeF_2,[33] and its behavior may provide interesting information about exciton-phonon scattering and allow to measure the excited-state Debye-Waller factors which are very difficult to measure by other techniques.

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