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# $Fe^{57}$ hfs and Néel Temperature in $Fe_xZn_{1-x}F_2$

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It is shown, using the Mössbauer effect of $Fe^{57}$, that the Néel temperature in the system $Fe_xZn_{1-x}F_2$ is proportional to the iron concentration for $0.25 \leq x \leq 1$. The results are in general agreement with the cluster-variation theories of Sato, Arrott, and Kikuchi, as well as with that of Elliott and Heap. The isomer shift and quadrupole splitting are independent of composition, indicating that the electronic wave functions are largely unaffected by changes in the metal-ion environment. The hyperfine field decreases linearly with the addition of zinc, ranging from 330.5 kOe in $FeF_2$ to an extrapolated value of 276 kOe in $ZnF_2$. The origin of this shift is discussed.

THEORIES of diluted magnetic systems were initially developed for metallic alloys. A detailed discussion of the susceptibility and critical temperature obtained from a number of models has been given by Sato, Arrott, and Kikuchi.[1] The Néel temperature in a dilute ionic system, $Mn_xZn_{1-x}F_2$, has been obtained by Baker, Lourens, and Stevenson[2] using the disappearance of the $F^{19}$ nuclear magnetic resonance (MNR) as an indicator of the attainment of long-range order. The theoretical discussion of these results led to the conclusion that the ratio of nearest-neighbor to next-nearest-neighbor exchange is greater than unity, a result which is incompatible with direct measurements as well as with theory.[3]

The Mössbauer effect of $Fe^{57}$ provides an opportunity to examine the Néel temperature in a closely related system, $Fe_xZn_{1-x}F_2$. Both systems have the rutile structure and Néel temperatures close to that of liquid nitrogen. A necessary prelude to the measurement of Néel temperature itself is an examination of the hfs of $Fe^{57}$ both above and below the ordering temperature. Pertinent information concerning some members of the series has been previously published,[4–6] and is generally in agreement with the measurements reported here.

## EXPERIMENTAL

The absorbers used in these experiments were in the form of crushed powders prepared from quenched polycrystalline melts of high-purity $FeF_2$ and $ZnF_2$. The compositions quoted were obtained by x-ray fluorescence analysis on the samples used.[7] The Mössbauer spectrometer has been previously described.[8] The radioactive source consisted of $Co^{57}$ diffused into palladium. Positive Doppler velocity corresponds to higher energy in the absorber. Temperature was measured by using a Au (Co 2.1%)-versus-Cu thermocouple calibrated at the temperature of liquid He, $H_2$, and $N_2$; and controlled by using a nichrome heater and a mica disk, variable thermal resistance.

## RESULTS AND DISCUSSION

### A. Hyperfine Structure

Above the Néel temperature the Mössbauer absorption spectra of polycrystalline absorbers of $FeF_2$ as well as of the mixed crystals consist of two lines of equal intensity and width, Fig. 1. The linewidth of all samples was the same within the experimental uncertainty, 0.028±0.001 cm/sec. This result is unexpected since the environment of an iron atom changes with the substitution of zinc. In addition to the obvious change in the occupancy of the next-near-neighbor sites there is a change in lattice constant, Table I. The lack of change in the linewidth with composition provides a sensitive preliminary indication that the isomer shift and electric quadrupole interactions are not dependent on composition.

The isomer shift at room temperature taken as the shift of the point half way between the two lines, Table II, displays no significant trend with composition.

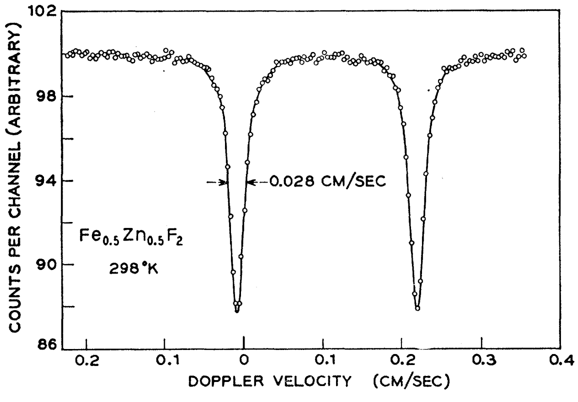

FIG. 1. Mössbauer-effect absorption spectrum of $Fe^{57}$ in $Fe_{0.5}Zn_{0.5}F_2$ at 298°K. The source is Pd($Co^{57}$) at 298°K.

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[1] H. Sato, A. Arrott, and R. Kikuchi, J. Phys. Chem. Solids **10**, 19 (1959).

[2] J. M. Baker, J. A. J. Lourens, and R. W. H. Stevenson, Proc. Phys. Soc. (London) **77**, 1038 (1961).

[3] R. J. Elliott and B. R. Heap, Proc. Roy. Soc. (London) **265**, 264 (1962).

[4] G. K. Wertheim, Phys. Rev. **121**, 63 (1961).

[5] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).

[6] G. K. Wertheim and H. J. Guggenheim, J. Chem. Phys. **42**, 3873 (1965).

[7] The authors are indebted to J. E. Kessler for these measurements.

[8] G. K. Wertheim, *Mössbauer Effect, Principles and Applications* (Academic Press Inc., New York, 1964), Chap. II.

TABLE I. Lattice parameters of $FeF_2$ and $ZnF_2$.[a]

| | | $FeF_2$ | $ZnF_2$ |
|---|---|---|---|
| Lattice parameters | $a$ | $4.6966_2$ | $4.7034_2$ |
| | $c$ | $3.3091_1$ | $3.1335_3$ |
| Metal-F | | 2.122, 1.993 | 2.038, 2.022 |
| Metal-Metal | | 3.7103,[b] 3.3091 | 3.6764,[b] 3.1335 |

[a] J. W. Stout and S. A. Reed, J. Am. Chem. Soc. **76**, 5279 (1954), and J. W. Stout and R. G. Shulman, Phys. Rev. **118**, 1136 (1960).
[b] Antiferromagnetic coupling.

The isomer shift below the Néel temperature is not given because it is difficult to obtain unambiguously from spectra which have broadened lines, and line intensities which depend on mixing ratios. (It could be computed as the centroid of the whole absorption but experience shows that small errors in the hypothetical zero-resonant absorption curve, as well as an anisotropic recoil-free fraction can produce excessive error.) The shift at 78°K in $Fe_{0.5}Zn_{0.5}F_2$, 0.131±0.001 cm/sec, is close to the low-temperature value in the system which may be taken as 0.137 cm/sec. The shift of 0.014 cm/sec between room temperature and 78°K is almost exactly the same as that found in metallic iron and is due to the second-order Doppler effect arising from the thermal motion of the atoms; it has no chemical implications.

The lack of variation of isomer shift with composition shows that the radial wave functions of the iron atom remain unchanged. The isomer shift, which measures the electronic charge density at the nucleus, is sensitive to changes in the covalency involving the $3d$ and $4s$ electrons. The absence of change in isomer shift indicates that this parameter is fully determined by the immediate fluorine environment, a result in accord with the usual theoretical treatment.

The quadrupole splitting which arises almost entirely from the $3d$ electrons of the iron atom itself is 0.282±0.002 cm/sec, at room temperature, Table I. It is also independent of composition. The 78°K value deduced from the $Fe_{0.5}Zn_{0.5}F_2$ data is 0.305±0.002 cm/sec. The value at 4.2°K in $ZnF_2{:}Co^{57}$ is 0.313±0.002 cm/sec. This value is significantly larger than that obtained from the analysis of the low-temperature magnetic data on $FeF_2$ (see Ref. 4) but the present value is considered to be more reliable. The temperature dependence of the quadrupole splitting is compatible with the theory due to Ingalls[9] who expressed the quadrupole splitting in the form

$$\Delta E=(2/7)e^2Q(1-R)\langle r^{-3}\rangle F(\Delta_1,\Delta_2,\lambda,T),$$

where $(1-R)$ is a Sternheimer shielding factor and $F$ is a reduction factor which contains the effect of spin-orbit interaction and of higher lying crystal field states.

TABLE II. Summary of experimental results.

| | $I.S.$[a] (cm/sec) | $Q.S.$[b] (cm/sec) | $H$[c] (kOe) | $\Gamma$[d] (cm/sec) | $T_N$ (°K) |
|---|---|---|---|---|---|
| $FeF_2$ | 0.118 | 0.280 | 330.5 | 0.029 | 78.2±0.2[e] |
| $Fe_{0.96}Zn_{0.04}F_2$ | 0.116 | 0.279 | 326.5 | ··· | ··· |
| $Fe_{0.762}Zn_{0.238}F_2$ | 0.118 | 0.282 | 316 | 0.027 | 58.4±0.3 |
| $Fe_{0.515}Zn_{0.485}F_2$ | 0.118 | 0.284 | 302 | 0.028 | 39.7±0.5 |
| $Fe_{0.259}Zn_{0.741}F_2$ | 0.118 | 0.284 | 290 | 0.029 | 19.3±1.0 |
| $Fe_{0.005}Zn_{0.995}F_2$ | 0.116 | 0.282 | ··· | ··· | ··· |
| $ZnF_2(Co^{57})$ | 0.117 | 0.281 | (276)[f] | ··· | ··· |
| Average | 0.117±0.001 | 0.282±0.002 | | | |

[a] Isomer shift at 298°K relative to $Co^{57}$ in Pd at 298°K.
[b] Quadrupole splitting at room temperature.
[c] Hyperfine field from splitting of ground state at 4.2°K.
[d] Linewidth at 298°K.
[e] This result is less precise but in agreement with that of Catalano and Stout [J. Chem. Phys. **23**, 1803 (1955)] who obtained 78.35±0.02°K.
[f] Extrapolated value.

Barring an accidental cancellation, the absence of change in $\Delta E$ with composition shows that $\langle r^{-3}\rangle$ as well $F$ remain unaffected, i.e., that the radial part of the $3d$ wave function of the iron atom as well as the low-symmetry components of the crystal field splitting of $Fe^{2+}$ in $ZnF_2$ and $FeF_2$ are essentially the same.

The magnetic hfs splitting, Fig. 2, on the other hand, exhibits obvious composition-dependent features. The data were taken at 4.2°K, well below the Néel temperature of even the 25% Fe sample so that they adequately represent the sublattice saturation magnetization.

The data for pure $FeF_2$ clearly show, in addition to the familiar six lines, two weak lines which arise because the magnetic substates of the excited nuclear state are mixed by the nonaxial electric field gradient (EFG) tensor. The hyperfine field is 330.5 kOe, somewhat smaller than the value previously obtained by extrapolation from 45°K.[4]

The substitution of zinc produces two effects; (1) the outer lines broaden by a factor of about 4 and (2) the average hf field decreases. The line broadening apparently arises from the existence of a range of values for the effective field. This suggests that it depends on the occupancy of the metal ion sites surrounding each iron atom. The average effective field can nevertheless be accurately determined from the ground-state splitting which moreover is independent of quadrupolar effects. The average field exhibits a linear decrease with composition, Fig. 3. This behavior is compatible with a model in which neighboring zinc atoms reduce the field by definite amounts which depend on their distance from the iron atom. Under these circumstances, assuming simple superposition

$$H(n_1,n_2,\cdots)=H_{FeF_2}\left(1-\sum_{i=0}^{\infty}a_in_i\right),\quad 0\leq n_i\leq Z_i$$

where $i$ denotes a shell of metal neighbor, $Z_i$ the number of atoms in that shell, $n_i$ the number of zinc atoms in that shell, and $a_i$ is a coefficient which measures the reduction per zinc atom. The average field $\bar{H}$, is readily computed on the assumption that the site occupancy is random, yielding

$$\bar{H}=H_{FeF_2}(1-\alpha c),$$

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[9] R. I. Ingalls, Phys. Rev. **133**, A787 (1964).

where $c$ is the atom fraction of zinc and

$$\alpha=\sum_{i=0}^{\infty} a_i Z_i.$$

The value of $\alpha$ derived from the data in Fig. 3 is 54.5 kOe.

The average field, of course, does not yield any information on how the various shell contribute to $\alpha$. This information is contained in the line broadening which is relatively large indicating that at most a small number of shells are involved. The trial assumption that only the eight equivalent sites which have the largest (antiferromagnetic) exchange interaction with the iron atoms need be considered accurately accounts for the line broadening, yielding both the proper magnitude and concentration dependence.

Although a large number of mechanisms contribute to the hyperfine field in $FeF_2$[10] it can be shown that most of them are likely to make only minor contributions to the change in field arising from the substitution of zinc.

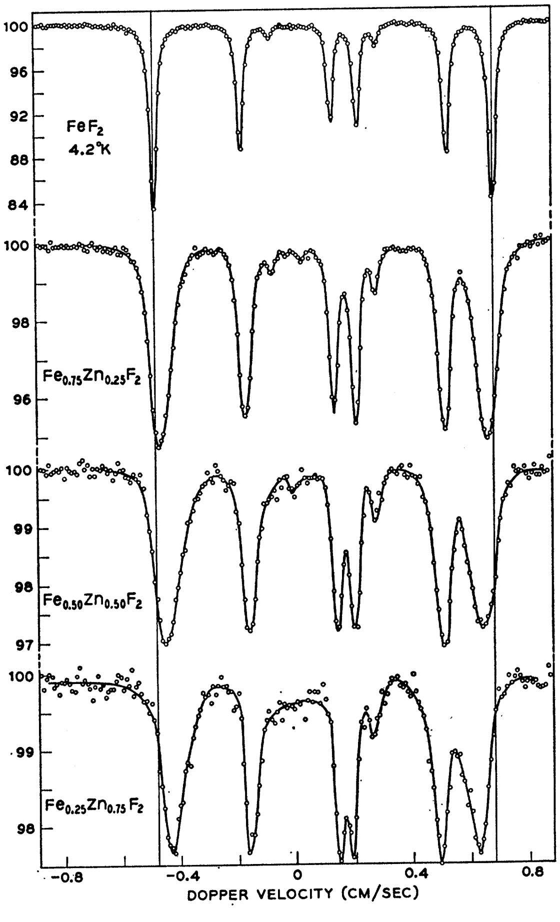

FIG. 2. Mössbauer-effect absorption spectrum of $Fe^{57}$ in $FeF_2$ $Fe_{0.75}Zn_{0.25}F_2$, $Fe_{0.50}Zn_{0.50}F_2$, and $Fe_{0.25}Zn_{0.75}F_2$ at 4.2°K, well below the Néel temperature.

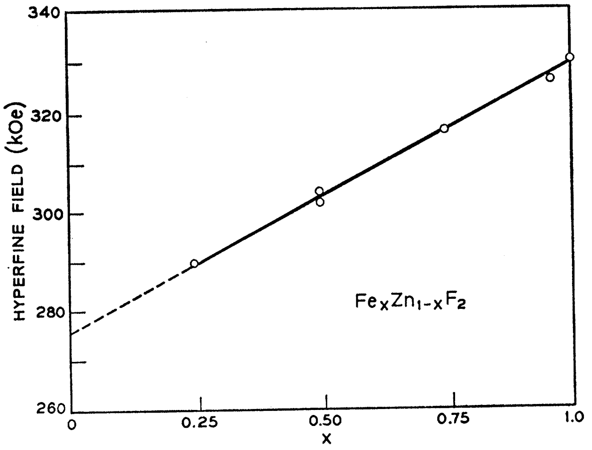

FIG. 3. The saturation value of the effective magnetic field at $Fe^{57}$ nuclei in the system $Fe_xZn_{1-x}F_2$.

The largest contribution to the hyperfine field is due to core-polarization. The finding that $\langle r^{-3}\rangle$ is independent of composition based on the constancy of the quadrupole splitting as well as the lack of significant variation in the hyperfine field per spin of $3d$ ions in general indicate that this term will make a negligible contribution to the observed shift. Dipolar interaction with the electronic magnetic moment of the neighboring metal ions is estimated to be an order of magnitude smaller than the observed effect. A significant contribution could arise from the transferred hyperfine interaction with the neighboring metal ions via the fluorine ligands, but its magnitude is uncertain. The most likely origin of the observed shift lies in the orbital term,

$$\mathcal{H}_{\rm orb}=2\mu_B\langle r^{-3}\rangle(g_z-2)\langle S_z\rangle,$$

where it arises from a change in $g_z$. Using the parameters in Ref. 10 the observed shift corresponds to a change in $g_z$ of about 0.05. The $g$ value of $FeF_2$ has been found to be $2.25\pm0.05$,[11] and that of $Fe^{2+}$ in $ZnF_2$, 2.24.[12] The $g$ shift required to attribute the entire observed change in hyperfine field to the orbital term is thus just within the experimental uncertainty of the two independent determinations. If a significant part of the shift arises from other causes such as the intra-atomic dipolar term[10] or the transferred hyperfine interaction the agreement will be improved.

### B. Néel Temperature

It is generally recognized that the Mössbauer effect provides an effective tool for the determination of the magnetic-ordering temperature. In ferromagnets it is advantageous because measurements can be carried out in zero field; in antiferromagnets because it allows a direct measurement of the sublattice magnetization. In the system under study the disappearance of the *un-*

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[10] A. Okiji and J. Kanamori, J. Phys. Soc. Japan **19**, 908 (1964).

[11] R. C. Ohlmann and M. Tinkham, Phys. Rev. **123**, 425 (1961).

[12] M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535 (1956); **A236**, 549 (1956).

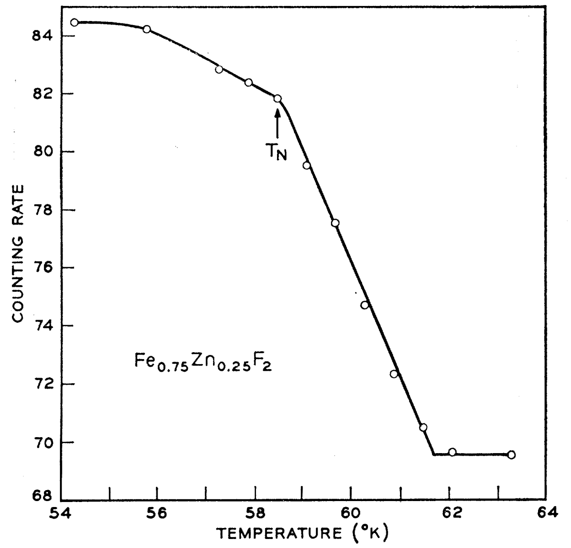

FIG. 4. Determination of the Néel temperature from the transmission of $ZnF_2(Co^{57})$ radiation through an $Fe_{0.75}Zn_{0.25}F_2$ absorber. No Doppler shift is employed.

*broadened* quadrupole doublet characteristic of the paramagnetic state was taken as the criterion for the onset of long-range order, i.e., the Néel temperature.

Two techniques were employed. (1) the absorption spectra of powdered $Fe_xZn_{1-x}F_2$ absorbers were obtained at various temperatures near the Néel temperature. The strength of the narrow doublet was plotted against temperature and extrapolated to zero intensity. In these experiments the sample temperature was deliberately allowed to fluctuate by ±0.1°K about the control point in order to smear out the spectrum of the magnetically ordered phase whose splitting is a very rapid function of temperature near $T_N$,

$$H(T)=H(0)D(1-T/T_N)^\beta ,$$

where[13]

$$D\sim 1.3 , \quad \beta\sim 0.33 .$$

This method gives a detailed picture of the approach to long range order, but is relatively tedious.

The second approach is based on the finding that the quadrupole splitting and isomer shift in $Fe_xZn_{1-x}F_2$ are independent of $x$, and on the earlier finding[6] that divalent $Co^{57}$ in $ZnF_2$ decays to divalent $Fe^{57}$, i.e., that electron capture after-effects disappear rapidly compared to the $10^{-7}$ lifetime of the first excited nuclear level of $Fe^{57}$. A source prepared by diffusing $Co^{57}$ into $ZnF_2$, mounted in contact with the $Fe_xZn_{1-x}F_2$ absorber in an isothermal enclosure provides a simple technique for obtaining the Néel temperature. When the absorber is in the paramagnetic state its absorption lines coincide with the emission lines of the source and the transmitted counting rate is low. When the absorber is magnetically ordered the counting rate is high. Data obtained by this technique are shown in Fig. 4. As the temperature is lowered the counting rate rises steeply as short-range order sets in; at the Néel temperature the slope changes because the quadrupolar doublet has been replaced by magnetically broadened doublet which then continues to spread out into the eight hfs components.

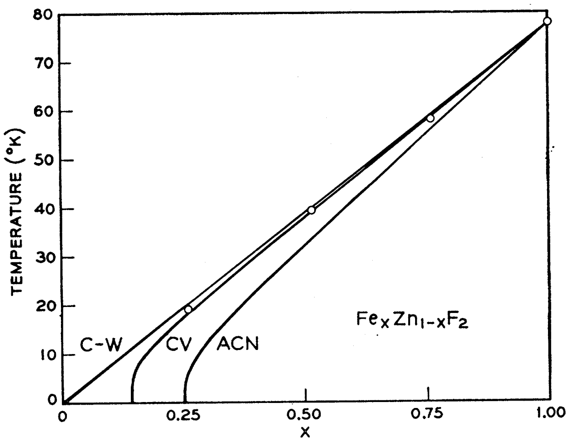

FIG. 5. Néel temperature in the system $Fe_xZn_{1-x}F_2$ as measured and according to the Curie-Weiss, cluster-variation, and average-coordination-number theories.

The results obtained by the two techniques are in good agreement and are plotted against composition in Fig. 5, which also shows the results of the three theoretical treatments discussed in Ref. 1. It is apparent that the data are in good agreement with the cluster-variation (C-V) method. The Curie-Weiss or molecular field method is valid only at high concentrations of the magnetic atom where it agrees with the C-V method. The results cannot be reconciled with "average coordination number" predictions. The experimental results may be summarized by saying that in the range from 0.25 to 1.00 atom fraction the Néel temperature is proportional to the concentration of magnetic atoms.

The reason for the difference of the behavior of $Fe_xZn_{1-x}F_2$ and $Mn_xZn_{1-x}F_2$ is not understood. The values of $J_1$ and $J_2$ for $FeF_2$ are $\sim$1.4 and $-2.6$°K,[11] not very different from those of $MnF_2$, 0.32° and $-1.76$°K.[14] The measured Néel temperatures are in good agreement with the theory for the rutile structure of Elliott and Heap[3] which for $|J_1/J_2|<1$ yield results very similar to the cluster-variation approach.

## ACKNOWLEDGMENTS

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[13] G. K. Wertheim, J. Appl. Phys. (to be published).

[14] G. G. Low *et al.*, J. Appl. Phys. **35**, 998 (1964).