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Temperature Dependence of the Fe^{57} hfs in FeF_2 below the Néel Temperature*

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The temperature dependence of the Fe^{57} hfs in FeF_2 has been obtained with the Mössbauer effect in the antiferromagnetic region. Data just below the Néel temperature yield a critical exponent $\beta=0.325\pm0.005$ and $D=1.36\pm0.03$. This value of β differs slightly from that of 0.333 ± 0.003 found in MnF_2 by Heller. However, this latter value also provides an adequate fit to our data, but over a more restricted range of temperature. D is larger than previously reported in other materials because of the larger magnetic anisotropy in FeF_2. In the low-temperature region (0–50°K), the present measurements are in good agreement with the more precise determination of the temperature dependence of the F^{19} NMR by Jaccarino, indicating that both measurements reflect the sublattice magnetization.

INTRODUCTION

THE study of thermodynamic variables in the vicinity of a critical point is a subject of current interest.[1] Considerable attention has been given to the temperature dependence of the magnetization near the Curie or Néel point, both from the theoretical[2–6] and experimental points of view.[7–14] It is generally found that the magnetization below the critical point may be expressed in the form

$$M(T)=M_0D(1-T/T_N)^{\beta}. \tag{1}$$

The important parameter is the critical exponent β. The coefficient D is introduced because the range of validity of this expression is limited to a region near the critical point, so that the magnetization at $T=0$ given by this expression is not equal to the measured value M_0. Recent experiments have given $\beta\sim0.33$ for a wide variety of substances although some significant deviations are on record. It has also been shown that this value emerges from suitable theories.

From the experimental point of view, the work of Heller and Benedek is of particular interest because they achieved higher precision in their work on MnF_2 than has been obtained in other cases. The critical exponent was found to be 0.333 ± 0.003 before correction for thermal expansion. It is of interest to examine whether this exponent depends on such factors as the magnetic interaction between ions or the crystallographic arrangement of the magnetic ions. It is very fortunate that isostructural FeF_2 makes it possible to examine a case where only one of these variables is changed. Both fluorides have the rutile structure.[15]

The magnetic anisotropy of FeF_2 is very much greater than that of MnF_2, reflecting the fact that the latter is an S-state ion while the former is not.[16] For the present purpose this is best thought of in terms of the energy required to excite a magnon in these two materials. In MnF_2, this magnon gap is ~13°K, much smaller than the Néel temperature[7] (67.336°K), while in FeF_2 it is 76°K, i.e., almost as large as the Néel temperature. The effects of this difference on the sublattice magnetization well below the critical point have been demonstrated by Jaccarino and Walker[17] who showed that magnetization of MnF_2 drops much more rapidly than that of FeF_2 as the temperature is raised from 0°K.

In this paper we will examine the behavior of FeF_2 in the vicinity of the Néel point and make a comparison with the data of Heller and Benedek for MnF_2.

EXPERIMENTAL

The material used in this investigation was prepared by H. J. Guggenheim of our laboratory. Mössbauer absorption spectra showed that the concentration of

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[1] See, for example, Natl. Bur. Std. (U. S.) Misc. **273**, 1 (1966).

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[14] See also a brief review by J. J. van Loef, Solid State Commun. **4**, 625 (1966).

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[16] J. W. Stout and L. M. Matarrese, Rev. Mod. Phys. **25**, 338 (1953).

[17] See V. Jaccarino [in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. 2A, pp. 307–355] for further discussion of the magnetic properties of these materials as well as for a comprehensive list of references.

trivalent iron was much less than 1 mole%. The data showed some distortion due to iron in the beryllium windows of our Dewar which prevented a more precise determination of Fe^{3+}. Although the FeF_2 was available in single-crystal form, all measurements were carried out with crushed powders since no advantage obtains from the use of oriented material in the present experiment. Single-crystal spectra were reported some time ago,[18] and were used to confirm that the hyperfine effective field H_{eff} is in the c direction in the ordered state, i.e., in the direction of the iron magnetic moments.

The measurements in the critical region were made with the sample immersed in liquid nitrogen in a Dewar having low-temperature beryllium windows. Care was taken to avoid contamination of the nitrogen by atmospheric oxygen. The temperature of the liquid nitrogen was controlled by varying its vapor pressure, using a Cartesian diver manostat. A stability of ±0.5 Torr was achieved corresponding to a temperature stability of ±0.005°K. The liquid nitrogen was in the inner chamber of a double Dewar. The outer chamber was also cooled with liquid nitrogen when temperatures below the normal boiling point of nitrogen were required, but it was not cooled for temperatures above 77.4°K. It was found that thermal equilibrium in the liquid bath was rapidly attained after a decrease in the pressure, but quite slowly after an increase because of a lack of convective mixing. Most data were consequently taken at a sequence of decreasing temperatures.

Temperatures below the triple point of liquid nitrogen were obtained using a partially thermally isolated cold finger in the Dewar vacuum space. Measurement and control were based on 2.1% Co in Au-versus-Cl thermocouples. The uncertainty in the temperature here was ~1°K but the data in this region do not contribute to defining the critical-point behavior.

The Mössbauer-effect spectrometer is similar to one previously described,[19] except that the current amplifier has been replaced by a Philbrick current booster placed within the feedback loop. This, together with an increase in the low-frequency cutoff of the integrator eliminates a tendency toward drift in the neutral position of the Doppler modulator. The frequency stability of the function generator was ±1 part in 10^4 and the calibration constant of the spectrometer is stable to ±1 part in 10^3 for many months.

The velocity calibration was based on the hfs splitting of high-purity iron. The source consisted of Co^{57} in palladium. The linewidth obtained with the inner lines of a 0.0025-cm-thick, high-purity natural iron absorber was 0.023 cm/sec. The isomer shift of this source relative to sodium nitroprusside (National Bureau of Standards standard #725) is 0.0441±0.0005 cm/sec.

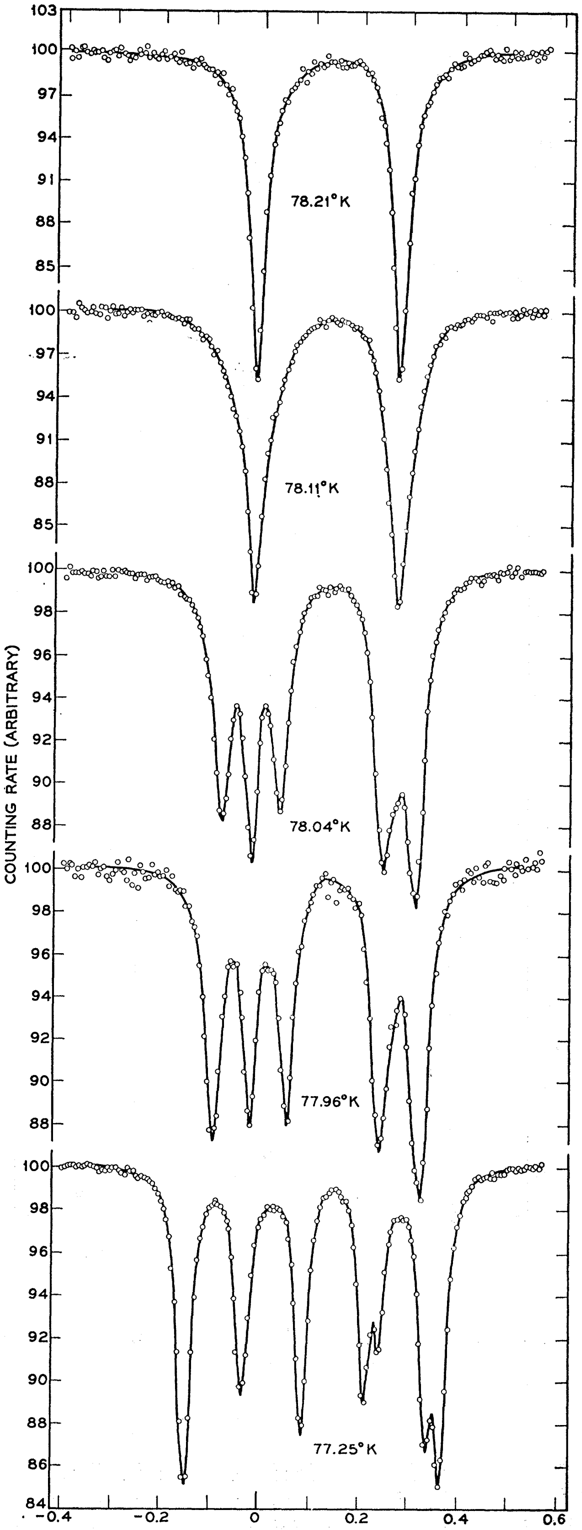

FIG. 1. Hyperfine structure of Fe^{57} in FeF_2 within 1°K of the Néel temperature. The data shown are from a run not included in Table II.

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

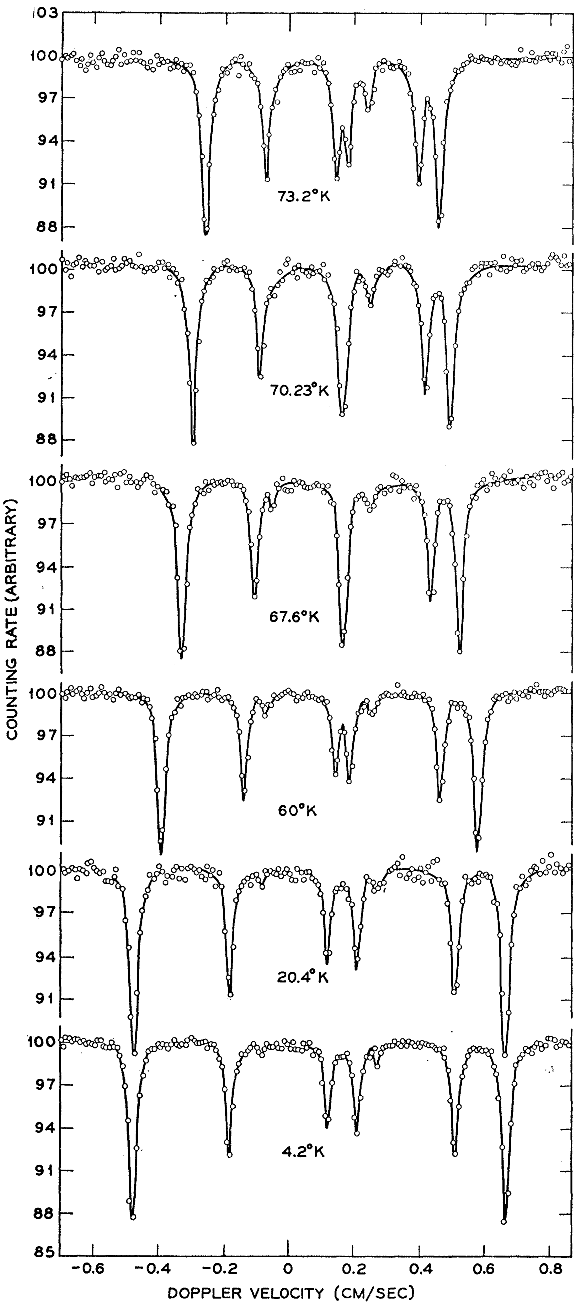

FIG. 2. Hyperfine structure of Fe^{57} in FeF_2 well below the Néel temperature.

RESULTS AND DISCUSSION

Examples of data obtained are shown in Figs. 1 and 2. The data in Fig. 1 cover a range of temperature of 1°K, in the immediate vicinity of the Néel point, and those in Fig. 2 the rest of the range down to 4.2°K.

It has been shown previously that the largest component of the asymmetric electric field gradient (EFG) tensor in FeF_2 is at right angles to H_{eff} which is along the c axis.[18] The smallest component of the EFG tensor is along the c axis. With this information, the hfs at 4.2°K was analyzed in detail to obtain the effective field, the quadrupole splitting, and asymmetry parameter.[20] The positions of all eight lines were first determined from the experimental data, with a probable error of 0.1 channel. The average of these eight line positions gives the isomer shift (see Table I). The splitting of the ground state was then obtained from the separations of four pairs of lines, yielding an effective field of 329±2 kOe.

The splitting of the excited state was then compared with machine calculations using a program due to H. H. Wickman of our laboratory. A two-dimensional search in quadrupole splitting Q.S. and asymmetry parameter η was carried out. (It is convenient to use the quadrupole splitting $\frac{1}{2}e^2qQ[1+\frac{1}{3}\eta^2]^{1/2}$ rather than e^2qQ as one of the parameters because its value can be obtained above the Néel point and is not expected to change appreciably with temperature.) Good agreement was found for a quadrupole splitting of 0.285 cm/sec and an asymmetry parameter of 0.40. The fit with 0.280 and 0.290 cm/sec was distinctly worse, but the value of the asymmetry parameter for best fit was the same. Changing the asymmetry parameter to 0.3 or 0.5 increases the rms error by a factor of about 5. We also investigated the effect of varying the value of H_{eff} by ±0.6%, the maximum amount compatible with the determination. The value of the quadrupole splitting and η remained unchanged.

As a final check, the whole spectrum was computed using $H=329$, Q.S.$=0.285$, and $\eta=0.40$. A comparison of theoretical and experimental line positions gave an rms deviation between theory and experiment in 0.00085 cm/sec, just less than the 0.1 channel uncertainty in the original determination of line positions. The line intensities are also in good agreement with the theory. The results are summarized in Table I. They

TABLE I. Summary of isomer-shift and hyperfine-structure parameters at three selected temperatures. 78.21°K is slightly above the Néel temperature.

Temp. (°K)	I.S.[a]	Q.S.[b]	η[c]	H_{eff}[d]
298	0.118_1[e]	0.279_1	...	0
78.21	0.129_1	0.292_1	...	0
4.2	0.129_1	0.285_5	0.40_2	329_2

[a] Isomer shift in cm/sec expressed relative to a Pd(Co^{57}) source at 298°K. The data given may be converted to the National Bureau of Standards sodium nitroprosside standard by adding 0.0441±0.0005 cm/sec.
[b] Quadrupole splitting in cm/sec, $\frac{1}{2}e^2qQ[1+\frac{1}{3}\eta^2]^{1/2}$.
[c] Asymmetry parameter.
[d] Hyperfine effective field in kOe.
[e] Subscripts denote probable errors in the last significant figure.

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[20] For explicit expressions applicable to this case, see K. Ono and A. Ito, J. Phys. Soc. Japan **19**, 899 (1964).

are more precise than an earlier determination[18] but are in reasonable agreement with it.

The quadrupole splitting is seen to be only weakly temperature-dependent with an indication of a decrease at low temperature. Such behavior has been previously described by Ingalls who showed that it arises from the effects of spin-orbit coupling.[21]

The details of the behavior in the region where the effective magnetic field is small can be used to obtain an independent estimate of the asymmetry parameter. In the case of Fe^{57}, a splitting of the two components of a quadrupolar doublet into a triplet and a doublet indicates that the magnetic field is perpendicular to the z direction defined by the EFG tensor. (If the EFG tensor has axial symmetry, one component splits as $2g\beta H$ while the other component remains unsplit as long as $g\beta H/e^2qQ \ll 1$ and $\mathbf{H}\perp z$.) The data show that the splitting of one level is approximately 1.6 $g\beta H$, while that of the other is 0.4 $g\beta H$. For $\eta=0.40$, the corresponding values are 1.58 and 0.42, but this determination is not very sensitive. Values from 0.35 to 0.45 give acceptable spectra.

For the present purpose it is not necessary to analyze all the data in detail. It suffices to deduce the splitting of the ground state since it is a direct measure of the sublattice magnetization. It can be obtained without accurate knowledge of the properties of the EFG tensor or the excited-state moments. For this purpose we have made a least-squares fit to the data using a Lorentzian line shape. The maximum number of lines in the data is eight. These are readily seen at some temperatures, e.g., Fig. 2, 60°K. (All eight transitions are allowed because the wave functions of the excited state are mixed by the asymmetric EFG tensor.) To assure convergence of the least-squares procedure, it was carried out with a number of lines no greater than those clearly resolvable in the data. The ground-state splitting, reported as an effective magnetic field in Table II and Fig. 3, is then directly obtained as the separation of four pairs of lines.

TABLE II. Summary of the hyperfine effective-field data. The temperatures quoted for sample immersed in liquid nitrogen were stable to ±0.005°K. The absolute accuracy of the temperatures has not been established. The hyperfine fields have probable errors of ±0.6%.

Temperature (°K)	Effective field (kOe)	Temperature (°K)	Effective field (kOe)
78.29	0	74.76	161.8
78.12	0	74.00	174.6
78.08	39.7	72.76	188.0
78.02	50.3	71.35	201.8
77.94	62.1	73.2[a]	182.3
77.85	70.5	70.2[a]	210
77.74	80.0	67.6[a]	231
77.54	92.0	60.0	272
77.28	103.0	50.0[a]	297
76.70	122.0	35.0[a]	319
76.09	137.4	20.4[a]	328
75.45	152.4	4.2[a]	329

[a] Sample in vacuum space.

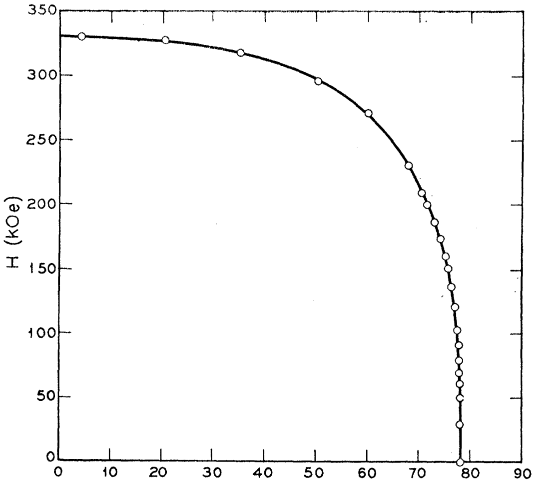

FIG. 3. The hyperfine effective field as a function of temperature.

In the region from 0 to 50°K, the data are in good agreement with the more precise results of Jaccarino[17] based on the F^{19} NMR. This agreement offers confirmation that these diverse quantities provide a measure of the sublattice magnetization.

The critical exponent is determined by fitting Eq. (1) to the data. The simplest procedure is first to extract T_N from an extrapolation of H^3 versus T to $H^3=0$ using only data in the immediate vicinity of the Néel point. The parameters D and β are then obtained from a plot of $\log_{10}H$ versus $\log_{10}(T_N-T)$. It should be recognized, however, that this procedure necessarily prejudices the determination in favor of $\beta=\frac{1}{3}$. In order to remove this objection, we have made such plots using a small range of values for T_N in the vicinity of that determined by the extrapolation procedure. Fortunately, the range of values which need be considered is greatly restricted by the data. The H^3 extrapolation yields $T_N=78.12$°K (Fig. 4). Data at 78.110± 0.005°K show small but significant magnetic broadening indicating that the Néel temperature is no lower. Plots made with T_N assumed to be 78.11, 78.12, and 78.13°K give slopes of 0.325, 0.333, and 0.34. The best fit over the widest temperature range is obtained with 78.11°K (Fig. 5). That at 78.13 is restricted in temperature range and distinctly inferior. We conclude that the best values are $T_N=78.11$°K, $\beta=0.325$, and $D=1.36$. However, the values $T_N=78.12$°K and $\beta=0.333$ also provide an adequate fit. The results,

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

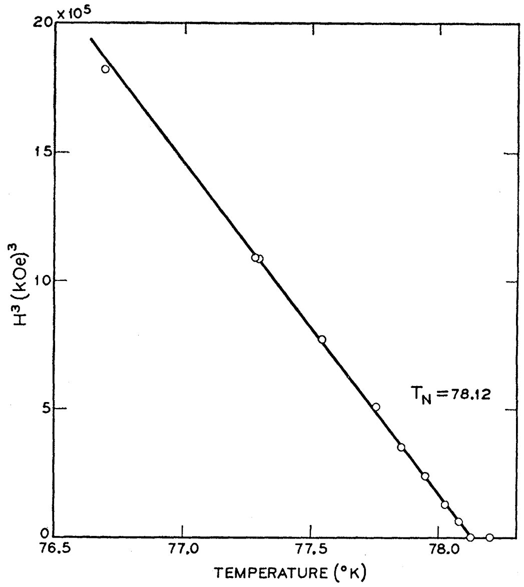

FIG. 4. Determination of the Néel temperature by extraplation.

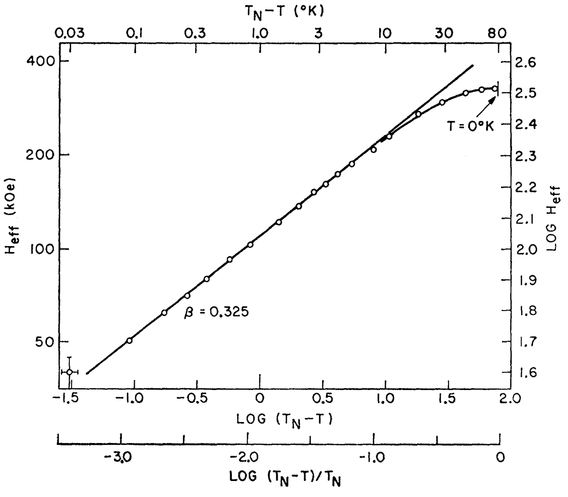

FIG. 5. Plot of $\log_{10} H_{eff}$ versus $\log_{10}(T_N-T)$ with $T_N=78.11°K$. The errors are no larger than the plotted points except for the single point closest to the Néel temperature, where they are shown explicitly.

therefore, do not show any significant difference between the critical exponents of MnF_2 and FeF_2.

A comparison of the reduced sublattice magnetization as a function of reduced temperature for the two substances, Fig. 6, shows that at equivalent temperatures the magnetization of FeF_2 is always closer to the saturation value. This is in accord with expectations based on the low-temperature behavior in which the reduced sublattice magnetization of FeF_2 always falls above that of MnF_2. In terms of the parameters in Eq. (1), the difference arises largely, if not entirely, through the coefficient *D*.

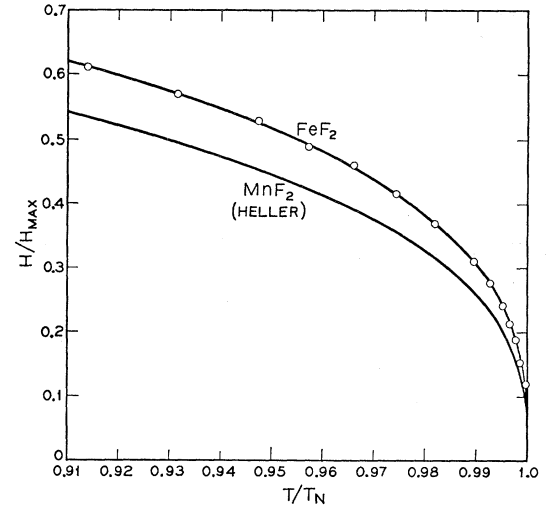

FIG. 6. Comparison of the sublattice magnetizations of MnF_2 (Ref. 7) and FeF_2 on a reduced plot. In spite of the major difference in this presentation, the critical exponents do not differ significantly.

The present results show that the critical exponent, in the case of two isostructural fluorides, does not vary significantly as the anisotropy of the magnetic interaction is changed. A similar value for the exponent has also been reported for compounds with NaCl [8] and perovskite [10] structure, but a significantly different exponent has been reported for $CrBr_3$.[12] It remains of interest to explore the factors determining this exponent in a systematic way.