over a wide range of wavelengths, and by providing inhomogeneous internal fields by the choice of irregularly shaped samples. Some mode overlap must remain because of exchange and will contribute to the echo decay by dephasing the echo components.

We would like to acknowledge valuable assistance of Mr. Steve Ichicki in these experiments.

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CRITICAL-POINT MAGNETIZATION OF AN IMPURITY IN AN ANTIFERROMAGNET

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The magnetization of Fe^{2+} in MnF_2, measured in terms of its magnetic hfs interaction, exhibits a critical exponent β equal to that of the host lattice. The large change in the coefficient D is ascribed to the effects of anisotropy and to the difference between the Fe-Mn and Mn-Mn exchange.

It is well known that the temperature dependence of the magnetization of a spin impurity in a magnetic solid may be quite different from that of the host. This effect can be demonstrated within the confines of molecular-field theory and arises whenever the impurity spin or its coupling to the molecular field differs from that of the host atoms. This effect has also been treated from the point of view of spin-wave theory.[1] However, neither of these two approaches provides a valid description of the temperature dependence of the magnetization of a pure substance in the critical region.[2] The behavior of an impurity in that region is therefore best approached by comparing it with the behavior of the host lattice.

For this experiment we chose MnF_2 as the host lattice because its critical behavior has been more thoroughly analyzed than that of any other magnetic material,[3,4] and Fe^{2+} as the impurity because it can be studied by Mössbauer effect. A recent examination of the magnetization of Fe^{2+} in MnF_2 in the spin-wave region[5] showed that the impurity magnetization drops much more slowly with increasing temperature than the magnetization of the host. This effect arises because the Fe-Mn exchange is larger than that between Mn atoms and also because of the greater anisotropy of the D-state impurity. The difference in spin, $\frac{5}{2}$ for Mn^{2+} and 2 for Fe^{2+}, also contributes. We here report the extension of these measurements into the critical region.

The experiment was carried out with MnF_2 into which radioactive $^{57}Co^{2+}$ had been introduced as a dilute impurity.[6] On the basis of the total activity, the crystal contained $\sim 10^{16}$ atoms/cm^3 of ^{57}Co. The cobalt decays by electron-capture to ^{57}Fe, which then emits the 14.4-keV gamma ray used in the Mössbauer-effect experiment. The spectrum was obtained with a conventional constant-acceleration spectrometer, using a single-line $K_4{}^{57}Fe(CN)_6 \cdot 3H_2O$ absorber. The MnF_2 sample was immersed in liquid nitrogen. Temperature was regulated by controlling the vapor pressure with a Cartesian diver manostat.

Experiments in the paramagnetic region show that the $^{57}Fe^m$ produced by the electron-capture decay of the divalent ^{57}Co is entirely in the divalent state when the Mössbauer gamma ray is emitted. This is in accord with the finding in a similar experiment on ^{57}Co in rutile structure ZnF_2.[7] The Mössbauer-effect hyperfine spectra obtained in the critical region are very similar to those in the critical region of FeF_2.[8] They were analyzed by fitting up to eight Lorentzian lines of adjustable position, width, and height to the spectrum. When possible, the hyperfine field was obtained from pairs of lines separated by the ground-state splitting. This has the advantage that the determination is independent of the quadrupole interaction of the excited state. In the immediate vicinity of the critical point, the resolution of such pairs is relatively poor. Here it becomes advantageous to use the two outer lines of the triplet (see Fig. 1 of Ref. 8), which are the only well-resolved lines of the spectrum. The three other lines consist of unresolved doublets. The hyperfine field was obtained from the complete expression for the hfs spectrum, using the quadrupole splitting measured in the paramagnetic state and the asymmetry parameter determined from low-temperature data. The data confirm that neither the quadrupole splitting nor the asymmetry parameter changes with temperature in the critical region.

The hfs effective field obtained from the above analysis is not necessarily a good measure of the magnetization of the impurity atom. If the hyperfine coupling constant is independent of temperature, then the dominant contribution to the effective field, which arises from core polarization, is proportional to the aligned spin. The orbital contribution need not have the same temperature dependence, and contributions due to transferred hfs will, in fact, have the same temperature dependence as the host lattice. Comparisons of ^{19}F NMR and Mössbauer experiments in the spin-wave region of FeF_2 showed, however, that the effective field at the ^{57}Fe is a good measure of the sublattice magnetization. On the assumptions that this is true also in the critical region and that transferred hyperfine fields make a relatively small contribution,[9] we will take the effective field as a measure of the impurity magnetization.

The results obtained are plotted in reduced form in Fig. 1. The MnF_2 sublattice magnetization is taken from the work of Heller.[3] The magnetization of the iron impurity is seen to rise much more rapidly than that of the host lattice, as might have been anticipated from the behavior in the spin-wave region.

The sublattice magnetization of the host is well represented by the equation[2]

$$M=M_0 D(1-T/T_N)^{\beta}, \tag{1}$$

with the parameters given in Table I. The behavior of the impurity implies either a reduction in β or an increase in D. The data (excluding the three points closest to the Néel temperature, whose probable errors are large) were analyzed by making a nonlinear least-squares fit to Eq. (1). The computer treats D, T_N, and β as independently adjustable parameters. The results are compared in Table I with the corresponding values obtained by Heller[3,4] in MnF_2 and by us in FeF_2.[8,10] We note first of all that the data yield a Néel temperature in good agreement with that reported by Heller in the pure substance. Secondly, the critical exponent β does not differ within the accuracy of the determination from that in either MnF_2 or FeF_2. This indicates that the effects of anisotropy and exchange on β are too small to be resolved by the present experiment, if not entirely absent. On the other hand, the coefficient D is very much larger than the corresponding value for the host lattice. One concludes in agreement with the work on FeF_2 that the major effect of anisotropy is to increase D. This has relatively little bearing on critical-point behavior, since it arises entirely from the flattening of the magnetization curve in the spin-wave region with increased anisotropy and exchange.

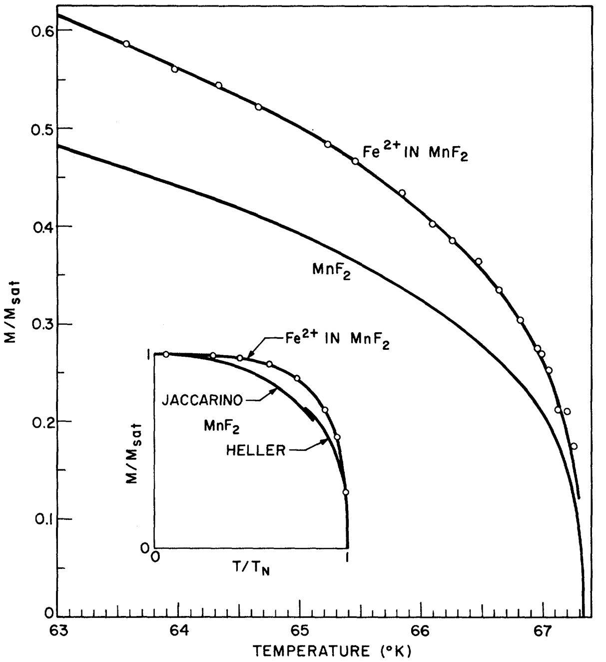

FIG. 1. Comparison of H/H_{sat} for Fe^{2+} in MnF_2 with the sublattice magnetization of the host determined by Heller from the nmr of ^{19}F, Refs. 3 and 4. H_{sat} is 227.5 kOe.

At first sight, it appears surprising that the impurity magnetization in the critical region is

Table I. Comparison of critical-point parameters in some rutile structure fluorides.

	Reference	β	T_N	D	Temperature Range
MnF_2	3	0.333(3)	67.336(3)	1.200(4)	0.92-0.99994
	4	0.336(6)	67.336		0.99-0.99994
Fe^{2+} in MnF_2		0.327(12)	67.34(4)	1.49(5)	0.94-0.999
		0.326(4)[a]	(67.336)	1.49(3)[a]	0.94-0.999
FeF_2	8, 10	0.325(5)	78.121(9)	1.37(3)	0.91-0.9995
	10	0.332(9)	78.125(9)	1.40(5)	0.95-0.9995

[a] Obtained by a two-parameter, least-squares fit in which T_N was set equal to 67.336°K. The errors quoted correspond to two standard deviations.

proportional to that of the host, when their temperature dependences are so different elsewhere, i.e., Fig. 1. It can be shown, however, that this result is expected on the basis of molecular-field theory. We assume that the magnetization of the impurity is given by a Brillouin function $B(x)$, where

$$x = \frac{g\beta S H_0 \langle M\rangle}{kTM_{\mathrm{sat}}}.$$

In the critical region where the temperature is large,

$$B(x) \sim \frac{(S+1)g\beta H_0 \langle M\rangle}{3kTM_{\mathrm{sat}}}.$$

Since $\langle M\rangle$ is singular at the critical point, the explicit temperature dependence can be neglected, showing that the impurity magnetization is proportional to that of the host. Explicit evaluation in which the molecular field is replaced by exchange with the eight next-nearest neighbors leads to an Fe-Mn exchange of 1.5 cm^{-1}, which is in agreement with other estimates.[11]

A second experiment was carried out with a mixed crystal containing 0.7 mole % $^{57}FeF_2$.[12] It was used as the absorber in a Mössbauer experiment in conjunction with a single-line ^{57}Co-in-palladium source. The data obtained with this absorber differ in a number of significant ways from those just discussed. Most apparent are a shift in the Néel temperature and line broadening in the immediate vicinity of the Néel point. Both indicate that the impurity concentration is sufficiently high to perturb the host lattice. The line broadening indicates that short-range order appears above the Néel point in iron-rich regions.

Least-squares analysis showed that the data could nevertheless be fitted by Eq. (1), with $T_N = 67.58 \pm 0.04$°K, $\beta = 0.316 \pm 0.008$, and $D = 1.45 \pm 0.06$, where the errors correspond to two standard deviations. Examination of the residuals shows no systematic temperature-dependent deviations. The increase in the Néel temperature is three times as large as expected on the basis of a linear interpolation between those of MnF_2, 67.336°K, and FeF_2, 78.12°K. The exponent obtained here should not be compared with that of the pure MnF_2. That of the impure host is not available for comparison. The interpretation of the behavior of such an inhomogeneous system requires an extension of present critical-point theories. The chief value of these last experimental results is to point up the fact that extremely high dilution is required if critical behavior is to be examined via an impurity atom.

The authors are indebted to L. R. Walker, S. Geschwind, and E. Helfand for helpful discussions.

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[9] The transferred hfs field in these compounds is usually estimated to be no larger than a few percent of the effective field. The origin of the large change in H_{eff} on Fe^{2+} in FeF_2 and MnF_2 is under investigation.

[10] The numerical results for FeF_2 in Table I are the results of a least-squares evaluation of the data of Ref. 8.

[11] This analysis was suggested to us by L. R. Walker.

[12] This sample was prepared from $^{57}Fe_2O_3$ which was first reduced to metal and then converted to FeF_2 by heating in flowing HF gas. The desired composition was obtained by melting together proper amounts of MnF_2 and $^{57}FeF_2$. The composition of the resulting material was verified by x-ray fluorescence analysis.

PHOTOEMISSION OF ELECTRONS FROM ALKALI AND ALKALINE-EARTH METAL CONTACTS INTO ANTHRACENE*

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The spectral yield for photoemission reveals the presence in the conduction band of anthracene of a broad (~0.65 eV) continuum of allowed states followed by four narrow ($\lesssim$0.1 eV) bands approximately 0.2 eV apart. The Fermi level in the alkali or alkaline-earth metal is fixed relative to the energy bands of anthracene by a large density of surface states. The mean free path for energetic electrons in anthracene is estimated as 40 Å.

Recently Williams and Dresner[1] have observed hole photoemission from several metal contacts into anthracene. The spectral response of the photoemission yield showed weak structure, suggesting that photoemission takes place into a system of narrow bands attributed to the interaction of molecular vibrations with a narrow electronic band. In this communication we report on electron photoemission from alkali and alkaline-earth metals into anthracene. The structure observed in the yield curves is much more pronounced in this case and provides some new information on the extensively studied structure of the conduction band of anthracene.

The specimens used were thin (30-90 μ) vapor-grown plates enclosed in sandwich-type cells. One face of the anthracene plate touches a transparent electrode, the other is in intimate contact with either a Na-K alloy or a mercury amalgam of the alkali or alkaline-earth metal. The metal is illuminated through the transparent electrode and the crystal, which are both transparent throughout the spectral range studied (1.5-0.44 μ). With a dc voltage applied (metal negative), appreciable photocurrents are observed. That these arise from photoemission from the active metal is established by the observation that the photocurrents for a pure mercury contact are at least one to two orders of magnitude lower.

Typical results for the spectral response of the quantum yield Y from three metal contacts into anthracene are shown in Fig. 1(a). Similar curves were obtained with Li and Ca amalgams. A striking feature of the data is the similarity in shape of all curves: The energy position of the threshold for photoemission ($E_T \approx 0.9$ eV) and of the various peaks are the same to within ±0.03

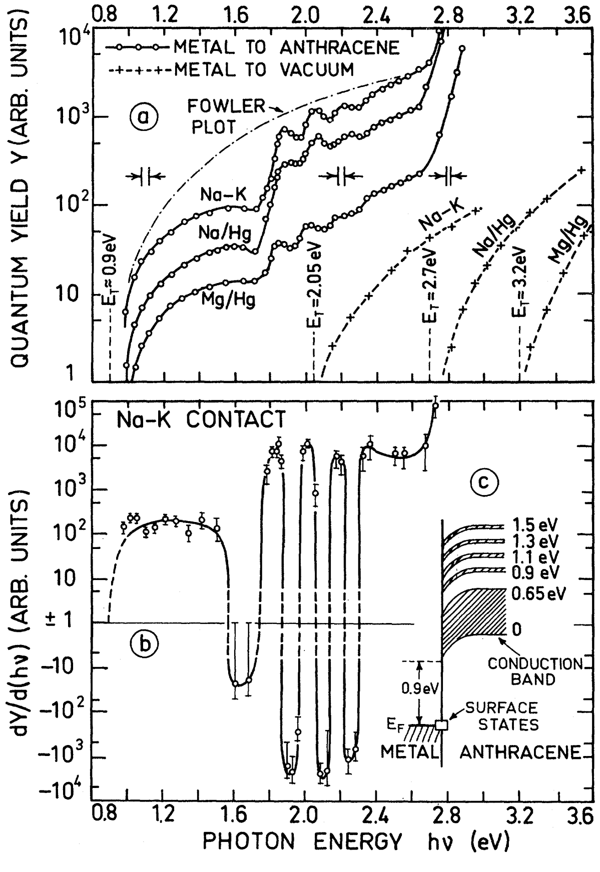

FIG. 1. (a) Quantum yield Y (electrons per incident photon) versus photon energy $h\nu$ for photoemission from Na-K alloy and from Na and Mg mercury amalgams into anthracene (solid curves) and into vacuum (dashed). (The two sets of curves are plotted on different yield scales.) Accuracy of data better than indicated by size of experimental points. (b) $dY/d(h\nu)$ vs $h\nu$ for the Na-K contact. Margin of error marked off for each point. (c) Energy band diagram at interface between alkali (or alkaline-earth) metal and anthracene.