Kondo Effect in Mo(Fe) Alloys from Mössbauer-Effect Measurements*

M. P. Maley† and R. D. Taylor
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544
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An extension of earlier Mössbauer-effect studies of the magnetic behavior of very dilute Fe impurities in Mo is reported. A connection is made between the well-known resistance minimum in this alloy and evidence for the transition to a nonmagnetic state at low temperatures. Consistent with current theories, based upon the s-d exchange model, a value of the characteristic Kondo temperature, T_K^{sd}, of (0.25 ± 0.05) °K is measured. Comparison with a recent spin-fluctuation model indicates $T_K^{sf} \simeq (1.0 \pm 0.1)$ °K. A field-dependent saturation hyperfine field is observed and determined to fit a recent theory by Ishii, which predicts an asymptotic approach of the low-temperature induced moment, with applied field, to its high-temperature value. The high-temperature moment is determined to be $\mu = 2.6\mu_B$. Implications for various physical models are discussed.

I. INTRODUCTION

Mössbauer-effect (ME) measurements of the magnetic hyperfine field at the site of Fe^{57} nuclei embedded as very dilute impurities in Mo metal matrices have been made. A temperature range of 0.4–300 °K was covered, while external magnetic fields, H, of 0–62 kOe were applied. As in previous measurements,[1] the magnetic response of the local moments centered on the Fe impurities is inferred from the behavior of the hyperfine field. The present work is an extension of an earlier ME study of the Mo(Fe) system.[1] A more detailed and systematic study of the low-temperature magnetic behavior of this alloy system is of interest in light of recent experimental and theoretical developments concerning the "Kondo-effect" anomalies observed in many magnetic and nonmagnetic alloys.[2] Mo(Fe) is of particular interest considering the fact that it exhibits a much-studied resistivity minimum,[3,4] which was cited among the first experimental demonstrations of the Kondo effect.[5] Current theory and several experimental studies[2] of other dilute alloy systems have associated with the resistivity anomaly a gradual transition to a low-temperature nonmagnetic state. In previous magnetic studies of Mo(Fe), authors have interpreted low-temperature deviations from paramagnetism either in terms of an older phenomenological model[1] or as evidence for magnetic ordering.[6] It is of interest, then, to study the low-temperature magnetic behavior of Mo(Fe) to characterize the nature of its low-temperature state. Previous measurements indicate that a low Kondo temperature, $T_K < 1.0$ °K, may characterize the system. This would make possible measurements in applied magnetic fields such that $\mu H > kT_K$ (μ is the magnetic moment of the impurity and k is Boltzmann's constant) and the possible destruction of the low-temperature Kondo state.

II. THEORY

A. General

Much current effort has been directed toward an understanding of the local moment problem in metals.[2,7] Recognition of the importance of many-body correlations in the electron gas interacting with an impurity potential has stimulated interest and has led to considerable progress. The original perturbation calculation by Kondo[5] demonstrated the existence of a divergence in the scattering amplitude of a conduction electron interacting with a localized magnetic moment via the s-d interaction, $\mathcal{H}_{sd} = -J\vec{S} \cdot \vec{s}$, where J is the strength of the exchange interaction, $\vec{S}$ is the impurity spin, and $\vec{s}$ is the conduction-electron spin density at the impurity. Subsequently, more exact "many-body" treatments of this problem have succeeded in removing the divergence, but have revealed the formation of "nonperturbative spin correlations" in the electron gas surrounding the impurity.[7-12] This has been interpreted by some authors as the formation of a "singlet bound state" between the impurity spin and a compensating cloud of conduction electrons.[8,10,13,14] The formation of this state has been shown to occur below a characteristic temperature for the alloy, $T_K = T_F e^{-1/|J|\rho}$ for negative exchange constant J, where ρ is the conduction-electron density of states at the Fermi surface and T_F is the Fermi temperature of the host metal.

Below this temperature, T_K, the Curie-like dependence of the susceptibility, χ, which characterizes the paramagnetic behavior of the impurities at higher temperatures, is seen to disappear and χ approaches temperature independence far below T_K. While current theories differ on the degree of compensation of the local moment, degradation

of the susceptibility to less than Curie dependence appears to be a general result of the calculations based upon the s-d exchange model. This behavior has been observed experimentally on a wide range of dilute alloy systems by susceptibility, NMR, and ME measurements.[2,7,15-18] The appearance of departures from paramagnetism has been correlated, for several alloy systems, with anomalies in the transport properties which are the salient features of the Kondo effect, and this success lends support to the theory. Doubt concerning this model has been raised following the observation by Suhl[19] that the question of the formation of a local moment could not be consistently separated from the problem of its interaction with the conduction electrons when this interaction proved to diverge in finite-order perturbation theory. This has led to calculations, based upon the Wolff model,[20] which treat the scattering of conduction electrons by a structureless impurity and which attempt to arrive at the formation of the impurity state and its magnetic behavior self-consistently.[21,22] One of the principal results of this approach has been the appearance of anomalies in the transport properties and in the magnetic behavior as a result of spin fluctuations in an alloy system which is nonmagnetic according to the Anderson criterion.[23] Thus, the low-temperature nonmagnetic behavior is seen as truly characteristic of the impurities, while the high-temperature paramagnetism is viewed as a strongly exchange-enhanced fluctuation which gives a Curie-like behavior[22] to the susceptibility when the fluctuations occur at a slower rate than ordinary thermal fluctuations. Under these circumstances, a magnetic moment which is temporarily in existence will have time to come into thermal equilibrium with the lattice in the presence of the field before vanishing. At lower temperatures, the thermal relaxation times become too slow for equilibrium to be established during a fluctuation, and a nonmagnetic behavior develops. This theory is not restricted to the nonmagnetic regime, and it predicts a smooth transition in physical properties, such as the susceptibility, as the coupling parameters vary through the magnetic limit.[21] However, the nonmagnetic or small fluctuation limit of the theory[22] yields simple, phenomenologically correct expressions for the physical properties, which are adequate for comparison with the present experimental results and which will be described below.

In the following discussion, physical properties which have been calculated on the model of a magnetic (in the Anderson sense[23]) moment interacting with the conduction electrons through the s-d exchange interaction will be denoted by the subscript sd. A subscript sf will be used in describing calculations based upon the spin-fluctuation model.

B. Low-Field Susceptibility

Perturbation calculations based upon the s-d exchange model at high temperatures ($T > T_K$) yield the expression for the susceptibility per impurity,[24]

$$\chi_{sd} = \left(\frac{\mu_e^2}{3kT}\right)\left(\frac{\ln(T/T_K)-1}{\ln(T/T_K)}\right) , \tag{1}$$

where μ_e is the effective moment per impurity in its environment. This expression is generally considered to be an accurate description of the magnetic response of a dilute magnetic alloy ($U/\Delta > 1$)[23] in a temperature range where the s-d interaction may be treated as a small perturbation. The same expression has been obtained as the high-temperature limit of the more exact Green's-function treatment[20] and appears to be characteristic of the high-temperature behavior of the s-d exchange model. As has been noted,[2] this expression is numerically equivalent for $4T_K \leq T \leq 100\ T_K$ to the Curie-Weiss form,

$$\chi_{sd} \simeq 0.81\mu_e^2/[3k(T+4T_K)] \tag{2}$$

to within a better than 1% accuracy.

Similarly, recent calculations[22] based upon the spin-fluctuation model give for the region $kT \gg \tau_0^{-1}$,

$$\chi_{sf} \simeq \mu_e^2/(4kT+\pi\tau_0^{-1}) , \tag{3}$$

where τ_0 is the spin-fluctuation period. This expression is considered to be valid in the region where thermal fluctuations occur at a faster rate than the quantum-mechanical fluctuations in the moment itself [i.e., the same region of interest as for Eq. (2)]. A Curie-Weiss form

$$\chi \simeq \mu_e^2/(T+\theta) \tag{4}$$

for the high-temperature susceptibility has been observed experimentally for a number of alloy systems.[2,7] From Eq. (2), it is evident that the s-d exchange model makes the association $T_K^{sd} \simeq \frac{1}{4}\theta^{sd}$ for the temperature characteristic of the singlet quasibound state formation. Correspondingly,[22] the spin-fluctuation theory makes the connection $\tau_0^{-1} \simeq kT_K^{sf}$, and thereby $\theta^{sf} \simeq (\pi/4)T_K^{sf}$.

Some question yet remains concerning the proper form for the low-temperature susceptibility ($T \ll T_K$). Singlet-ground-state models[13,14] generally yield an approach to a finite temperature-independent value, $\chi \simeq \mu_e^2/kT_K$, while the spin-fluctuation model predicts a similar behavior. However, some theoretical[25] and experimental[18] support exists for a divergent susceptibility at $T = 0\ ^\circ\mathrm{K}$ with a weaker than T^{-1} dependence. Quite generally, a smooth transition from the high-temperature Curie-Weiss–like behavior to near-temperature independence seems well established.

C. High-Field Susceptibility

An early perturbation calculation[26] based upon the s-d exchange model indicated the existence of a critical field, $H_K \simeq kT_K/\mu$, above which the spin-compensated state would be broken up, even at $T = 0\,^\circ\mathrm{K}$, and a return to paramagnetic behavior established. For lower values of the applied field, a constant low-temperature susceptibility would imply a linear dependence of the magnetization upon applied field. However, recent calculations based upon a ground-state singlet model have shown that applied fields many times larger than H_K are required before such a singlet state is completely destroyed.[27,28] Ishii[28] has calculated the magnitude of the local spin value induced by the magnetic field at $T = 0\,^\circ\mathrm{K}$. He finds that, as the applied field is increased from zero, the local spin is still partially quenched and asymptotically approaches the free-spin value at high field. The resulting expression for the impurity magnetization at $T = 0\,^\circ\mathrm{K}$ can be written as

$$\langle M\rangle = g\langle S_z\rangle \mu_B = \mu\,(\mu H)/[(\mu H)^2 + (kT_K)^2]^{1/2}, \tag{5}$$

where $\langle\,\rangle$ denotes time average, g is the Landé factor, μ_B is the Bohr magneton, and $\mu = g\mu_B S$ is the impurity moment.

D. ME Measurements

A microscopic measurement of the impurity magnetization may be obtained from a study of the magnetic hyperfine field at the Fe^{57} nucleus. In addition to the applied field H, the nucleus will see an internal hyperfine field H_i, which is assumed to be proportional to the electronic polarization localized on the impurity site. If the electronic relaxation times are much shorter than the Larmor precession time of the nucleus in the effective field, then we may write

$$H_i = H_{\mathrm{sat}}\langle S_z\rangle/S \simeq H_{\mathrm{sat}} M/M_0, \tag{6}$$

where $\langle S_z\rangle$ is the long-term time average of the electronic spin in the direction of H, and H_{sat} is the value of H_i when $\langle S_z\rangle = S$. For a free paramagnetic spin, this expression becomes[1]

$$H_i = H_{\mathrm{sat}}\, B_S(\mu H/kT), \tag{7}$$

where $B_S(x)$ is the well-known Brillouin function. Several recent attempts[1,16] have been made to modify Eq. (7) phenomenologically in order to account for the low-temperature Kondo-effect deviations to be expected on the basis of the susceptibility results discussed above. The most obvious modification can be made by incorporating the result of Eq. (4) for the high-temperature susceptibility leading to

$$H_i = H_{\mathrm{sat}}\, B_S[\mu H/k(T+\theta)]\ . \tag{8}$$

This expression should be consistent with the susceptibility measurements for $T \gg T_K$ and, together with them, provide independent measurements of H_{sat}, μ, and θ. However, at lower temperatures, difficulties with this form are to be expected. For $T \leq T_K$, there is no theoretical justification for Eq. (4) for χ. Furthermore, it is generally assumed that $H_{\mathrm{sat}} \propto \mu$. It has been suggested, on the basis of the ground-state singlet model, that μ is a function of T and H and should properly approach zero as H and T vanish. This has suggested the general form[16]

$$H_i(H, T) = f(H, T) H_{\mathrm{sat}}^0\, F[f(H, T)\mu^0 H/kT]\ , \tag{9}$$

where H_{sat}^0 and μ^0 are the high-temperature free-spin values of the respective parameters and $f(H, T)$ is a smooth function which approaches unity for μH or $kT \gg kT_K$ and which becomes zero for $H = T = 0$. F is a function which approaches a Brillouin function for $T \gg T_K$ and which describes the thermal distribution among whatever magnetic levels are available to the complex spin system. At low temperatures and high magnetic fields, this expression simply reduces to $H_i = f(H, 0) H_{\mathrm{sat}}^0$ if $F(x) \to 1$ for large enough values of the argument. This constitutes the assumption that whatever moment is induced by the applied field becomes completely polarized as $T \to 0$. A study of the hyperfine field at temperatures sufficiently low that thermal saturation is approached will thus allow a determination of the dependence of the induced moment magnitude upon applied field. A comparison can then be made with the theoretical predictions for this model [Eq. (5)]. Clearly, the ME measurement is considerably more model dependent than the susceptibility results. The possibility in the former of separating thermal-population effects, contained in $F(x)$, from changes in the magnitude of the moment, contained in $H_{\mathrm{sat}}(H, T)$, has led to several interesting speculations concerning the nature of the low-temperature state.[7,16]

Since $f(H, 0)$ describes the dependence of the ground-state moment upon applied field, it may clearly be related in the Ishii theory with Eq. (5). We will then have, combining Eqs. (5) and (9),

$$H_{\mathrm{sat}}(H) = H_{\mathrm{sat}}^0\, \mu H/[(\mu H)^2 + (kT_K)^2]^{1/2}, \tag{10}$$

where always $H_{\mathrm{sat}}(H)$ denoted the hyperfine field at zero temperature.

III. EXPERIMENTAL

The method of measurement is the same as has been reported.[1,29] The effective field H_{eff} acting on the Fe^{57} impurity nucleus is determined from the hyperfine spectra using the locations of the

(generally) well-resolved outermost pair of ME peaks. The effective field is taken to be composed of the applied field H, acting directly on the nucleus, and the internal field H_i induced at the Fe^{57} sites in the host material due to the localized moment. Other contributions to H_{eff} are taken to be compensatory and negligible compared to H and H_i. Experimentally, the average internal field is found to lie antiparallel to H. The negative sign is demonstrated by observing that $H_{eff}=H+H_i$ decreases with temperature in a constant applied field of, say, 62 kOe. For Fe in Mo, $H=-H_i$ at about 9 °K and 62 kOe, the spectra being unsplit, whereupon lower temperatures produce a hyperfine split pattern in which H_{eff} is negative due to the predominant contribution of H_i.

The spectra were analyzed graphically and by computer fits in order to obtain H_{eff} from the splitting. A few data were obtained from line broadening when the hyperfine spectra were not resolved. Weights were assigned to each datum to reflect the uncertainty of the determination of H_{eff}.

The apparatus used for these measurements has been described elsewhere.[1,29] Improved temperature regulation in the 4–300 °K range was accomplished by using a Keithley AR 150 microvoltmeter to measure the voltage across a carbon resistor attached to the sample holder. The out-of-balance signal was applied (after amplification) to a heater attached to the sample holder. Temperatures measured by means of a calibrated carbon resistor and/or a copper-constantan thermocouple were stable to better than 0.1% and accurate to better than 3%. Vapor-pressure measurements of He^4 or He^3 were used from 4 to 0.4 °K.

A 62-kOe superconducting solenoid, in which the Mössbauer source was centered, was operated in the persistent mode. The field was determined from the applied current which was measured to better than 0.1%. Uncertainty of the field strength was less than 1%.

The Mössbauer spectrometer was calibrated using either the source in the cryostat or a collimated unsplit source located coincident with the usual γ-ray path and an Fe absorber mounted on the room-temperature velocity transducer. Correction for a slight interaction of the drive with the solenoid was applied [$\Delta v/v \simeq (0.0004/\text{kOe})H$].

The ME technique allows measurements to be made on extremely dilute samples if one uses Mössbauer sources rather than absorbers containing the Mössbauer nuclide. In particular, 10^{-8} g of Co^{57}, the parent of Fe^{57}, is sufficient for reasonable counting rates. The source primarily used in this investigation was prepared from a 99.99+% spectroscopic-grade Mo rod (Johnson, Matthey and Company), which was rolled flat in a sealed Mo alloy container, machined to diameter, etched, and reanalyzed for magnetic impurities. This analysis gave an aggregate of 10–60 atomic ppm Fe, Co, and Ni. About 0.5 mCi Co^{57} Cl_2 activity was electroplated from a slightly ammoniacal solution onto a disk area of about 30 mm^2. The disk was heated in H_2+He in a furnace for about 3 h near 1500 °C followed by a vacuum anneal while cooling.

Pulse-height spectra of the 123-, 14.4-, and 6.4-keV photons from the source were taken before and after the diffusion treatment. The average depth of diffusion was determined from the relative attenuation by a procedure outlined previously.[1] The "average depth" of anneal determined was 2×10^{-2} mm, which ideally corresponds to ~16 atomic ppm Co^{57} added in the thin layer. Our estimate of the Fe and other Co isotopes added is less than 50 atomic ppm. The manufacturer's maximum total solids estimate for the solution used corresponds to 1700 ppm if all went into the layer; however, the plating and diffusion techniques should eliminate the bulk of these impurities, believed to be mostly organic resin from the isotope separation procedure. Thus, the total magnetic impurities present in the source used in these measurements was in the range 75–125 atomic ppm in the vicinity of the average Mössbauer nucleus. An autoradiograph of the surface showed the activity to be evenly distributed.

The concern with concentration stems from the fact that complications in the interpretation could arise if magnetic ordering were taking place at the lowest temperatures. Coles *et al.*[30] report evidence for a magnetic transition at 1.5 °K in a sample of Mo containing 4000 ppm Fe. The estimated concentration of the source being used in the present measurements is a factor of 40 times lower than Coles's sample, and, by extrapolation, should order at temperatures much lower than 0.5 °K.

While the measurements described in Sec. IV were all made on the single source described above, concentration independence was determined by comparison with previous ME studies of the Mo(Fe) system.[1] The sources studied in the previous work[1] covered the range 50–1500 ppm. The low-temperature behavior of all samples was identical, within experimental error, to that discussed in Sec. IV below. While insufficient data were taken in the prior study to determine accurately the parameters describing the low-temperature behavior, the agreement of the individual data with those presented here convincingly establishes concentration independence.

The ME method also serves as a direct means of detecting ordering. A spontaneous internal field of a few kOe is readily detectable as line broadening. The present measurements and the previous

ones[1] showed no evidence of ordering down to 0.4 °K.

The source used in this investigation has been employed in a detailed study[31] of the "temperature shift" of the γ ray and of its recoil-free fraction over the range 4–750 °K. No unusual behavior was found. We find that the shifts measured in an applied field agree with those reported.[31]

IV. RESULTS

In Fig. 1 are shown all of the data for the Mo(Fe) sample described above. The hyperfine field H_i at the Fe^{57} nucleus is plotted as a function of H/T in the usual manner. As discussed in Sec. III, the hyperfine field will be assumed to be proportional to the magnetization centered on the Fe site. The solid curve (marked 1) drawn through the high-temperature ($T \geq 19$ °K) points is a least-squares computer fit to Eq. (7), characteristic of free-paramagnetic-spin behavior. As is evident, this functional form provides a good description of the dependence of the magnetization upon H and T over the ranges ($0 \leq H \leq 62$ kOe) and ($\sim 6 < T \leq 300$ °K). However, for temperatures below ~ 6 °K, it is apparent that the magnetization is no longer a unique function of H/T and appears to be characterized by a different slope for each temperature. Curves 2, 3, and 4 represent similar fits to Eq. (7), each with correspondingly different values of the parameters μ, S, and H_{sat}. For $\mu H/kT < 1$, the slope of the Brillouin function is equal to $(S+1)\mu H_{sat}/3S$. The least-squares-fit values of this parameter are given for the four curves in the figure caption. Because of the probable field and temperature dependence of the individual parameters, no individual values have been quoted for the low-temperature fits. As is apparent, the initial slope has decreased

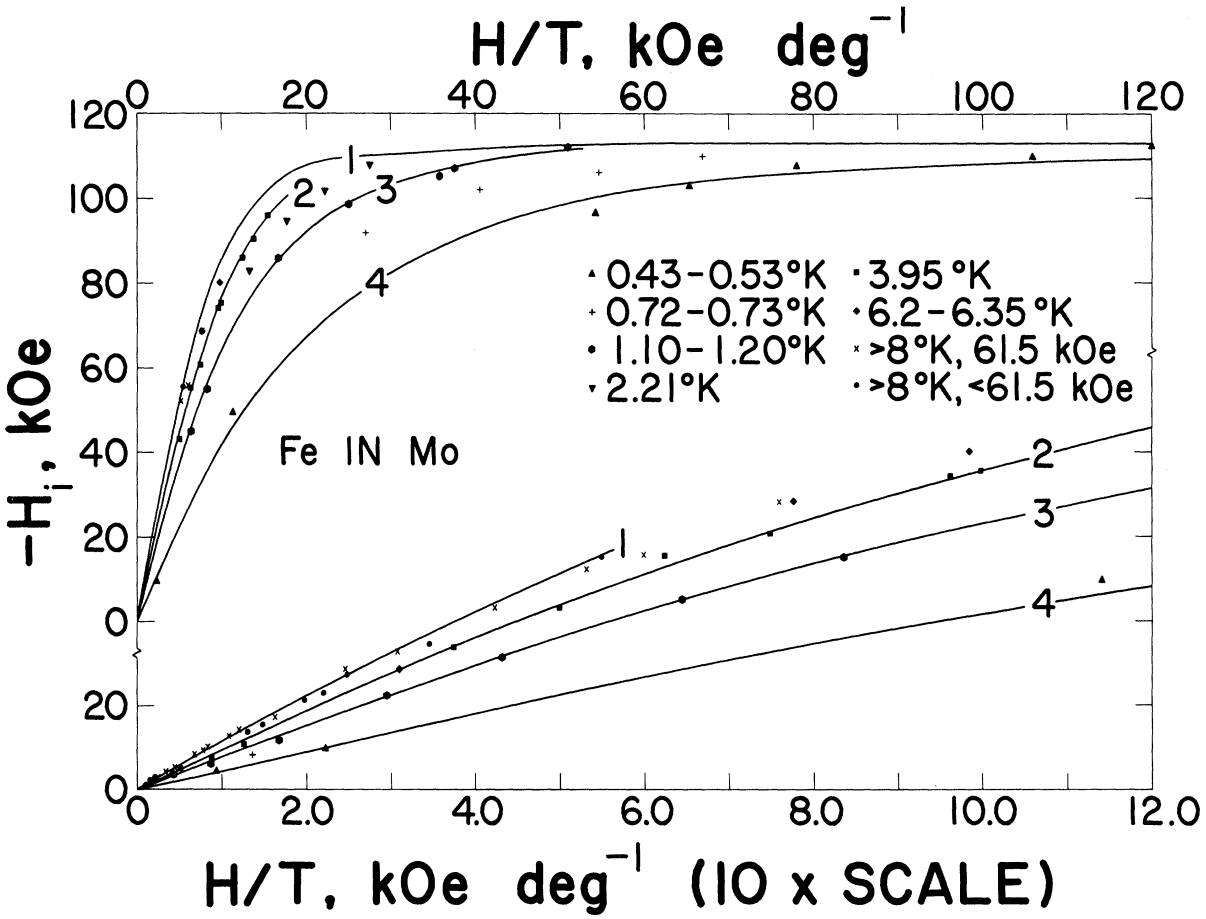

FIG. 1. Internal field H_i induced at very dilute Fe sites in Mo as a function of H/T. The data taken in various temperature intervals are identified. The numbered curves are least-squares fits of the data to a free-spin Brillouin function [Eq. (7)] using data selected as follows: (1) $T > 19$ °K, H_{sat} fixed = −113.5 kOe, (2) $T = 3.95$ °K, (3) $T = 1.10$–1.20 °K, (4) $T = 0.43$–0.53 °K. The low H/T data are shown in the expanded plot, and the initial slope, $(S+1)\mu H_{sat}/3S$, for each curve is −169, −138, −113, and $-66.4\mu_B$ kOe.

below half of its high-temperature value by 0.5 °K. If we assume a value of $H_{sat}^{0} = -113.5$ kOe (see discussion below) for the high-temperature data, a value of $\mu = 2.4\mu_B$ is obtained assuming $g = 2$. This value is consistent with the susceptibility result[6] of $\mu = 2.1\mu_B$ and with previous ME measurements.[1] In Table I we present tabulated values of the data shown in Fig. 1 along with weights which were assigned prior to data analysis.

In Fig. 2 is illustrated a best fit of the data to the Curie-Weiss functional form, Eq. (8), for a value of $\theta = 0.8$ °K. The general over-all fit appears to be quite good.

As discussed in Sec. III, this functional dependence is to be expected for $T > 4\ T_K$ for an alloy undergoing a Kondo transition to a spin-compensated state. However, two systematic deviations can be discerned. At high values of $H/(T + 0.8\ ^\circ\mathrm{K})$, the fit becomes rather poor. The source of this difficulty will be shown below to be related to an applied field dependence of H_{sat}. And, in the linear, low $H/(T + 0.8\ ^\circ\mathrm{K})$ region the lower-temperature points ($T \sim 0.5$ °K) can be better fitted with a $\theta \sim 0.5$ °K. This behavior is more clearly illustrated in Fig. 3, which is equivalent to a standard $1/\chi$ plot for the reciprocal of the susceptibility as a function of temperature. In this case we have plotted H/H_i versus T. This is simply related to the inverse susceptibility by

$$1/\chi = H/M = HS/\langle S_z\rangle\ \mu = (H/H_i)(H_{sat}/\mu). \quad (11)$$

The points displayed represent the data for $0.5 \lesssim T < 50.0$ °K, where sufficient accuracy in the determination of H/H_i is possible. Only data for which $H/T < 3$ kOe/°K are displayed in order to remain in the linear portion of the Brillouin function. In this region, Eq. (8) becomes

$$H/H_i = [3Sk/(S+1)\mu H_{sat}]\,(T+\theta)\ . \quad (12)$$

Since Eq. (8) is only expected to be valid for $T \gg T_K$, we have fitted the data for $4.0 = T \leq 50.0$ °K to Eq. (12). The solid line displayed represents a least-squares fit for the parameters: $\mu = 2.4 \pm 0.2\ \mu_B$ and $\theta = (1.1 \pm 0.3)$ °K. The lower-temperature points drop monotonically below this line with decreasing temperature. This gives $1/\chi$ a concave downward character in this region, in agreement with the more exact perturbation calculation for the susceptibility, Eq. (1). This behavior is consistent with the conclusion that points below 4.0 °K are sufficiently close to T_K that Eq. (8) is no longer a valid approximation for H_i. The value of $\theta = (1.1 \pm 0.3)$ °K is then judged to be properly representative of the high-temperature behavior.

In Fig. 4, we have plotted the data emphasizing the high H/T region near saturation and treating the constant applied field points separately. This is a similar analysis to that performed on Cu(Fe) ME data by Frankel *et al.*[16] and shows a similar field dependence of H_{sat}. As is apparent, the hyperfine field saturates thermally at a value which is a monotonically increasing function of H. The change in H_{sat} upon changing from H from 20 to 60 kOe corresponds to 40% of the change in applied field. This is much too large an effect to be explained by the usual Knight-shift mechanism. The curves drawn through the points represent least-squares fits to the Brillouin form Eq. (7). While

TABLE I. Experimental data: Observed hyperfine field H_{eff} is taken to be composed of the applied field H and the induced internal field H_i. The uncertainty in determining H_i is essentially that of determining H_{eff} and, for well-resolved spectra, corresponds to less than ±1 kOe. The accuracy of H and T are given in the text. The weights listed were assigned to reflect the uncertainty due to several factors involving counting statistics, drive stability, complex nature of some of the spectra and the quality of the curve fitting procedure to the spectra.

H	T	$-H_i$	Wt.	H	T	$-H_i$	Wt.
61.2	0.43	112.2	7	39.4	4.1	74.1	5
61.2	1.17	111.9	7	39.4	6.4	48.7	5
60.9	2.21	107.9	7	39.4	11.4	34.6	4
61.2	3.95	95.9	6	39.4	19.9	21.3	4
61.1	6.2	79.9	3	29.6	0.45	106.7	8
61.1	8.1	68.3	7	29.6	0.73	101.9	8
61.1	10.2	55.6	5	29.6	1.18	98.6	8
61.1	11.5	52.3	7	29.6	2.21	83.1	6
60.9	14.4	43	3	29.6	3.95	60.6	6
61.0	19.9	32.9	5	29.6	19.9	15.7	3
61.9	25.3	28.3	5	30.0	142	2.9	4
61.0	37.5	17.1	6	30.0	187	2.0	3
61.9	51	14.2	3	30.0	293	1.0	3
62.0	57	12.6	5	24.6	3.95	55.3	4
62.0	74	10.1	5	19.7	0.43	76.6	8
61.9	79	9.4	3	19.7	0.73	91.7	9
60.9	90	8.3	2	19.7	1.18	86.0	9
62.0	141	5.2	4	19.7	3.95	43.1	2
62.0	185	4.4	6	19.7	6.4	28.7	4
62.0	293	2.6	3	20.0	9.1	23.1	6
54.2	3.95	90.4	6	14.8	3.95	33.9	4
49.3	0.47	109.6	8	9.85	1.18	55.0	5
49.3	0.74	109.9	7	9.86	3.95	21.8	8
49.3	2.21	101.8	8	7.38	1.14	45.0	2
49.3	3.95	85.9	7	4.93	0.43	49.7	2
50.0	9.1	55.2	5	4.93	1.14	31.4	4
49.3	6.4	68.2	4	4.93	3.95	10.6	2
49.3	19.9	27.4	6	3.45	1.17	22.3	1
49.3	38	13.7	6	3.45	3.95	7.55	6
50.0	293	1.9	3	1.97	1.17	11.6	5
44.3	1.18	106.9	8	1.97	3.95	4.92	5
39.4	0.51	107.4	8	0.99	0.45	9.58	5
39.4	0.72	106.0	8	0.99	0.72	8.35	5
39.4	1.10	104.9	8	0.99	1.14	5.99	5
39.4	2.21	94.8	7	0.49	0.53	4.42	4
39.4	3.95	75.3	9	0.49	1.14	3.69	3

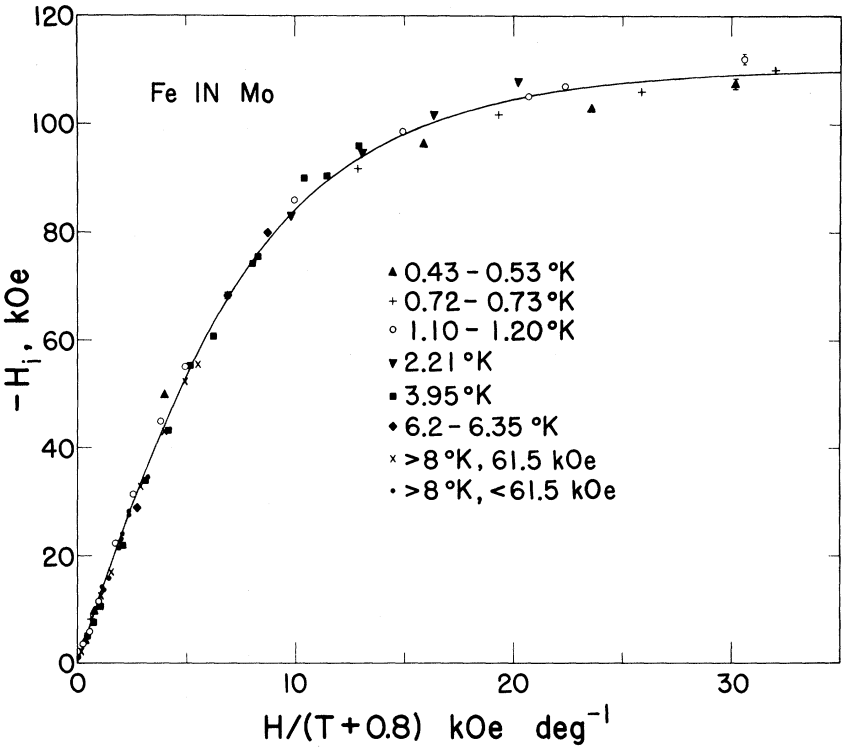

FIG. 2. Induced internal field H_i of ^{57}Fe impurities in Mo as a function of $H/(T+0.8\,°\mathrm{K})$. All the data are shown and are grouped by temperature or applied field H. Solid curve is the least-squares fit of Eq. (8). The initial slope is $-169.2\mu_B$ kOe. Certain systematic deviations are discussed in the text.

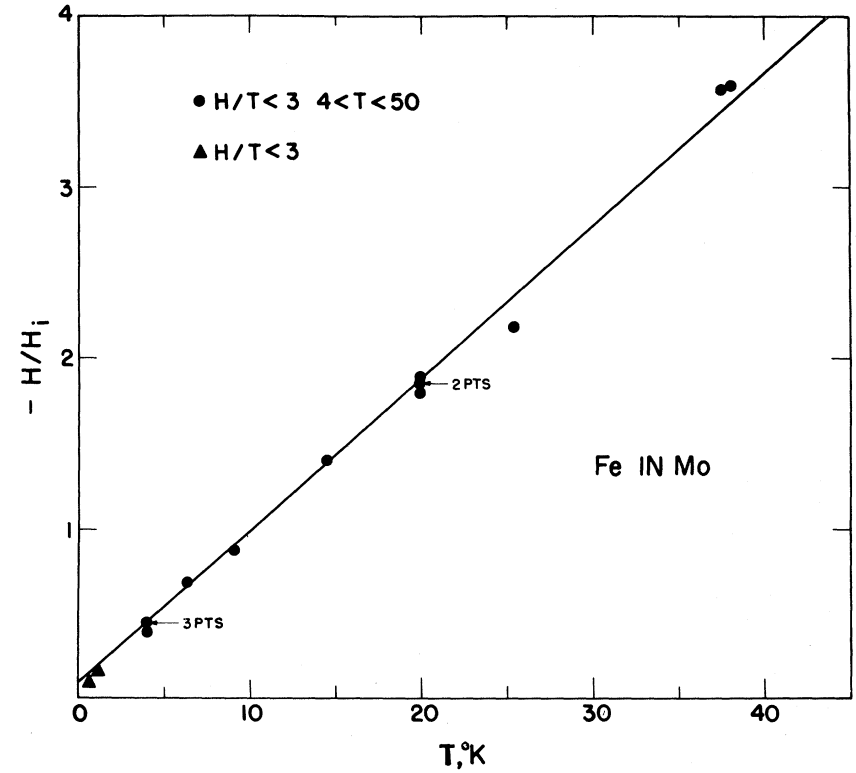

FIG. 3. H/H_i versus T for $T<50\,°\mathrm{K}$ and $H/T<3$ kOe °K^{-1}. $H/H_i \propto 1/\chi$. Low H/T ensures that the data are in the linear portion of the Brillouin function. The least-squares line results from minimizing the errors in $(H/H_i)^{-1}$, i.e., the reciprocal of Eq. (12), and is consistent with higher-temperature data. Triangles each represent three data points and were not included in the data fit. They serve to show the tendency of the low-T data to deviate systematically from the Curie-Weiss form (see text).

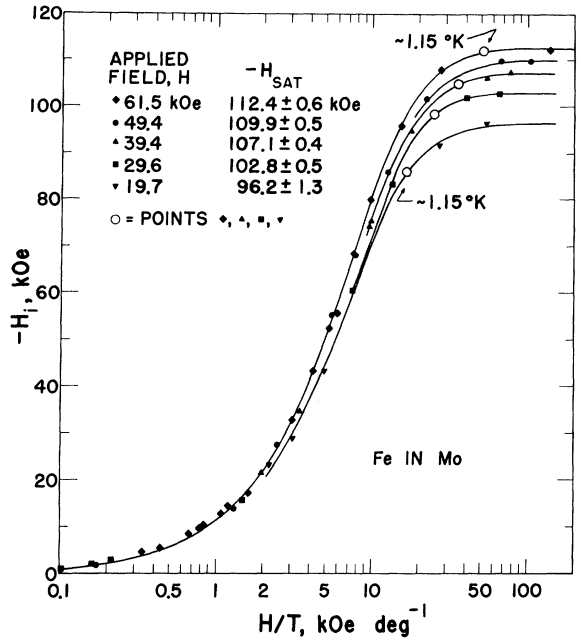

FIG. 4. Behavior of the ^{57}Fe internal field as a function of H/T at several fixed values of the applied field H. For each solid symbol the corresponding value of H and the resulting value of $-H_{sat}$, determined by fitting Eq. (7) to the isofield data, are listed. Solid lines represent those fits. Open circles locate the data where $T = 1.1 - 1.2$ °K.

no particular significance can be attached to these fits over such a wide range of temperature, the values of H_{sat} which are quoted in the figure were obtained as least-squares values for the lower-field curves. While the data for $H \geq 40$ kOe showed complete saturation by $T = 0.5$ °K, the two lower curves were extrapolated by means of the Brillouin fit. For applied fields < 20 kOe, the hyperfine field was still sufficiently far away from saturation at 0.5 °K that no accurate determination for H_{sat} could be made. It should be noted, however, that for $H = 5.0$ kOe at the lowest temperature, $-H_i = 50.0$ kOe. This represents a lower limit for $-H_{sat}$ (5 kOe).

As previously discussed, H_{sat} is presumed to be proportional to μ. The field dependence of H_{sat} can then be interpreted as evidence for a field induced moment which is approaching its high-temperature free-spin value from a low-temperature value of zero as H is increased. With this in mind, we have attempted to fit our determinations of H_{sat} versus H to the Ishii theory, Eq. (10). The results are shown in Fig. 5. The agreement is surprisingly good and yields a least-squares value for $T_K = 0.86$ °K/μ_B. Also, we arrive at a least-squares value for $H_{sat}^0 = -113.5$ kOe, which was used in determining μ^0 from the Brillouin fit.

The Mössbauer spectra from which these data were taken were, in general, well defined and uncomplicated. There was no observable broadening at zero applied field down to the lowest temperatures measured. However, below 6.0 °K, the spectra showed an anomalous strengthening of the center portion of the spectrum.[1] This added center strength is highly field dependent and has decreased considerably by 40 kOe. Splittings were taken from the outer pair of lines, which were generally well resolved and unaffected. However, at 2.0 °K and below, very anomalous spectra were observed for fields of 10 kOe and below. These were characterized by a very strong unsplit line in the center which was often twice as large as the outer pair which were considerably broadened. These spectra are very similar to ME measurements of magnetic systems which are undergoing relaxation effects.[32] This occurs when the electronic relaxation times become comparable with the Larmor precession time of the nucleus in the effective hyperfine field. An apparent superposition of at least two spectra from magnetically different sites is a possible description of the spectra.

V. DISCUSSION

The experimental results for Mo(Fe) reported above are largely consistent with the *s-d* model of a well-defined localized moment undergoing a transition to a spin-compensated nonmagnetic state at low temperatures. The data for $T \geq 4.0$ °K are best described by a Curie-Weiss form, Eq. (8), with $\mu = 2.4\mu_B$, $H_{sat} = -113.5$ kOe, and $\theta = 1.1$ °K.

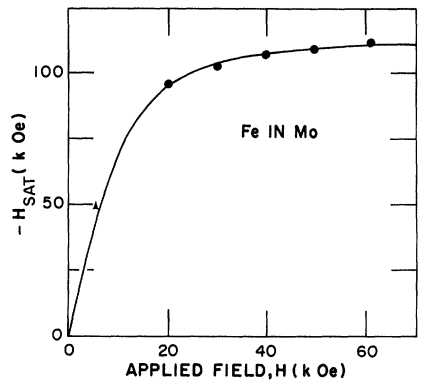

FIG. 5. Field dependence of H_{sat}. Values of $-H_{sat}$ versus H as determined in Fig. 4. The theoretical line is defined by Eq. (10). A measurement at 5 kOe is shown and is believed to be a lower bound to $-H_{sat}$ (5 kOe).

It is this high-temperature ($T > T_K$) behavior which is most unambiguously connected, through the theory, with the characteristic Kondo temperature T_K. The prescription $\theta \simeq T_K^{sd}/4$ implies $T_K^{sd} = (0.25 \pm 0.05)\,^\circ\mathrm{K}$. Likewise, comparison with Eq. (2) implies $\mu_{sd} = 2.67\,\mu_B$. This picture is corroborated by the resistivity measurements of Coles[3] which show the classic minimum and are consistent with $T_K^{sd} \simeq 0.25\,^\circ\mathrm{K}$.

Conversely, the high-temperature behavior of the hyperfine field makes no distinction between a spin-compensation and a spin-fluctuation model, since both now predict a Curie-Weiss behavior for $T > T_K$ [Eqs. (2) and (3)]. For $\theta = 1.1\,^\circ\mathrm{K}$, we find $T_K^{sf} = (4/\pi)\theta = 1.4\,^\circ\mathrm{K}$.

Comparison of these results can also be made with the susceptibility measurements of Knapp[33] on this same alloy system. While the susceptibility results indicate a somewhat lower value for T_K, the highest-temperature measurement reported is $4.0\,^\circ\mathrm{K}$. The downward slope of $1/\chi$ for our lowest-temperature points, noted in Fig. 3, will likewise lead to a lower value for θ if only $4.0\,^\circ\mathrm{K}$ and colder points are used in the extrapolation.

In order to make a convincing connection between the low-temperature measurements reported here and the Kondo effect, it is necessary to eliminate the possibility of antiferromagnetic order as a possible cause for the Curie-Weiss behavior of the magnetization. As discussed in Sec. III, since a concentration range of over 30 was covered among the three samples studied, with no observable change in θ, magnetic ordering cannot be an important consideration. The absence of any broadening in the single line at zero applied field at the lowest temperatures reached confirms this conclusion.

The observation of the field dependence of H_{sat} for the Mo(Fe) alloy system corroborates similar observations in Cu(Mn)[34] and Cu(Fe)[16] and leads to the conclusion that this effect is characteristic of Kondo-anomaly systems.

As previously mentioned, the apparently low value of T_K for the Mo(Fe) alloy facilitates measurements in fields for which μH is large compared to characteristic binding energies kT_K. Unfortunately, the present measurements do not extend into the region $T \ll T_K$ where the comparison with $T = 0$ theories becomes completely valid. However, the apparent saturation of our $0.4\,^\circ\mathrm{K}$ data indicates that we are close to $T = 0\,^\circ\mathrm{K}$ behavior, at least for $H \geq 40$ kOe. Comparison with the Cu(Fe) data also lends credence to our extrapolated results for H_{sat} for $H < 40$ kOe. At any rate, thermal effects at our lowest $T \simeq T_K$ would certainly tend to reinforce the breakup of a singlet magnetic state in high magnetic fields. The gradual asymptotic approach of $H_{sat}(H)$ to H_{sat}^0 is then in agreement with the Ishii singlet-state calculation. This result disagrees with the procedure of linear extrapolation of $H_{sat}(H)$ to H_{sat}^0 which has recently been applied to the Cu(Fe) data.[7]

Much current interest has been directed toward an understanding of the nature of the ground state of the impurity conduction-electron system. The ME measurements in Cu(Fe),[16] showing the effect of applied field upon H_{sat}, have recently been interpreted as evidence for the picture that only half of the measured low-temperature susceptibility arises from the moment located on the impurity.[35] Presumably, the localized part alone contributes to H_{sat}, while the remainder of the susceptibility comes from an extended spin polarization in the conduction band. This observation is based upon a comparison of low-temperature ($T \ll T_K$) susceptibility results and ME measurements on Cu(Fe). If at $T \simeq 0.0\,^\circ\mathrm{K}$, $\chi = \mu_{eff}^2/3kT_K$, then Eqs. (6), (7), and (11) give

$$H_i(H, 0) = H_{sat}(H) = H_{sat}^0\,\chi H/\mu^0 = H_{sat}^0[g(S+1)\,\mu_B/3kT_K]H. \qquad (13)$$

Comparison of the present measurements with this form may be made if we assume $T_K = 0.25\,^\circ\mathrm{K}$, $H_{sat}^0 = -113.5$ kOe, and $\mu = 2.65\mu_B$. For $H = 5$ kOe, Eq. (13) gives $H_{sat}(5\ \mathrm{kOe}) \simeq -25$ kOe. This value is about half the measured lower bound for $H = 5$ kOe, as mentioned in Sec. IV. From Fig. 5 the Ishii result for a singlet-state model appears to provide much better agreement.

While uncertainties by a factor of 2 in the assignment of T_K are not at all uncommon in current experimental work on Kondo-effect systems, the above result merits a few remarks. The result of the high-temperature measurements is that a value of $T_K = (0.25 \pm 0.05)\,^\circ\mathrm{K}$ for Mo(Fe) is consistent within the s-d exchange model. This value does not lead to a consistent connection between the predicted low-temperature susceptibility and the dependence of the saturated hyperfine field upon H. In this regard, the theory of Ishii, which prescribes an asymptotic approach to H_{sat}^0, seems adequately to describe the behavior of Mo(Fe). Furthermore, statements[7,35] concerning the percentage of the low-temperature susceptibility which contributes to H_{sat} do not appear to be appropriate for this system. It would seem appropriate to question the validity of the customary assumption $H_{sat} \propto \mu_{local}$ when the value of μ_{local} may be undergoing significant changes. Therefore, the fit of the data to the Ishii theory, while indicating the correct qualitative dependence, may not be significant for an accurate determination of T_K. In particular,

the least-squares parameters imply $T_K \simeq 2.0\,^\circ$K assuming a μ of $2.4\,\mu_B$. This value for T_K is much too large to be consistent with the high-temperature measurements.

Unfortunately, no high-field calculations for the spin-fluctuation model have yet appeared and no ready distinctions between it and the *s-d* exchange model can be made on the basis of the present magnetization data. In both models a gradual transition to nonmagnetic behavior below a characteristic temperature is predicted. The relaxationlike effects upon the ME spectra noted above appear to be characteristic of Kondo-effect systems[1] and seem to be more consistent with a model in which times of local moment magnitude fluctuation are becoming comparable with thermal fluctuations in the direction of the temporary moment. The interpretation of these spectra would then be important in establishing a physical description of the low-temperature nonmagnetic state.

VI. CONCLUSIONS

The present ME measurement on the Mo(Fe) alloy is interpreted as exhibiting the same sort of transition to a nonmagnetic state as has been observed in several other alloy systems. Application of current theories to the experimental results indicates a characteristic temperature $T_K^{sd} \sim 0.25\,^\circ$K on the *s-d* exchange model and $T_K^{sf} \sim 1.0\,^\circ$K on the spin-fluctuation model. Extension of ME, susceptibility, and resistivity measurements to lower temperature such that $T \ll T_K$ would be of considerable interest. In addition, a search at these temperatures for thermopower and specific-heat anomalies which have been observed in other Kondo systems would be of interest.

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†Present address: Department of Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, N.Y. 12181.

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Electron-Transfer States of Pairs of Unlike Transition-Metal Ions in Perovskite Fluorides

J. Ferguson* and H. J. Guggenheim

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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Experimental evidence is presented for the observation of electron-transfer bands between unlike transition-metal ions. Two examples are considered. First, the spectra of crystals of composition $KMn_xNi_{1-x}F_3$ and $KZn_{1-x-y}Mn_xNi_yF_3$ show an intense ultraviolet band (greater than 50 000 cm^{-1}) associated with electron transfer from nickel to manganese. Polarization data from $BaMn_{1/2}Ni_{1/2}F_4$ crystal spectra support this conclusion. Second, an electron-transfer band has been observed for the pair Cu − F − Mn in $KZnF_3$ crystals. The band is centered near 41 500 cm^{-1}, it is very broad with a long vibrational progression and it has an absorption intensity which increases on cooling of the crystal. These features can all be explained by the assignment $Mn^{2+}(3d^5)$, $Cu^{2+}(3d^9) \rightarrow Mn^{1+}(3d^54s)$, $Cu^{3+}(3d^8)$. It is concluded that this state determines the antiferromagnetic coupling in the ground state of the pair. A consideration of the possible electron-transfer states available to the pair when the manganese is in its excited $^4A_{1g}$ state provides an explanation for the observed ferromagnetic coupling of this state with Cu^{2+}.

I. INTRODUCTION

The theoretical interpretation of the antiferromagnetism exhibited by transition-metal ion crystals is extremely complicated, as can be seen from a recent discussion of the problem by Gondaira and Tanabe.[1] The main difficulty in the quantitative treatment of many electron ions lies in the large number of virtual states which enter into the calculation of the over-all exchange energy of the antiferromagnetic ground state. As these states are, in principle, accessible by direct absorption from the ground state, measurements of absorption spectra of these materials should be very valuable in sorting out the relative importance of the multitude of possible states. In practice, this is not easy because the spectral region concerned lies in the vacuum ultraviolet and, apart from an early study by Parkinson and Williams,[2] this region of the spectrum has not been examined at all. However, some of the difficulties can be eliminated if we turn our attention to the absorption spectra of unlike pairs of ions instead of concentrating on the pure materials.

The choice of crystal system is also another important factor because of the need to minimize the number and type of superexchange paths. The perovskite fluorides are particularly useful in this regard because of the simple nature of the exchange interaction through fluorine in a linear arrangement. The disadvantage is the lack of anisotropy in the absorption process because the crystal system is usually cubic. Earlier work has demonstrated that the exchange interaction between Mn^{2+} and Ni^{2+} leads to an enhancement of the absorption intensity of certain electronic transitions which are localized on either ion,[3] together with the appearance of new bands which correspond to the simultaneous electronic excitation of both ions.[4] It was speculated that the mechanisms of both types of absorption process involve primarily those virtual states for which there is electron transfer from nickel to manganese. The present paper presents experimental confirmation of this in the form of an intense ultraviolet absorption edge which can be assigned to this type of electron transition. In addition, a study has been made of the absorption spectrum of pairs of Mn^{2+} and Cu^{2+} in $KZnF_3$. A very broad band centered at 41 500 cm^{-1} has been found which can be assigned to the electron transfer from Cu^{2+} to Mn^{2+}. An assignment of this band is given and the nature of the states which determine the exchange energy is discussed.

II. RESULTS AND DISCUSSION

A. Nickel-to-Manganese Electron Transfer

It has been shown earlier[4] that there are two in-