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Kondo Effect and Localized Spin Fluctuations in the Zinc–3*d*-Transition-Metal System

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Very high-accuracy resistance measurements on dilute alloys of Mn, Cr, and Fe in zinc are presented. In all three systems the resistivity at high temperatures has a $\log_{10} T$ dependence but at the lowest temperatures of measurement a T^2 dependence is observed. The resistivity behavior is compared with the predictions of the $\vec{s} \cdot \vec{S}$ and the spin-fluctuation models. Measurements are also presented of the residual resistivity of the Zn–3*d*-transition-metal series extrapolated to $T = 0$ °K. It is found that the residual resistivity can be explained in terms of a model of an unmagnetized Friedel virtual bound state. Previous measurements on the zinc–3*d*-transition-metal series have been summarized in the Appendix.

I. INTRODUCTION

In the last few years there has been a great deal of experimental and theoretical work on those systems which show a logarithmic, or nearly logarithmic, anomaly in the temperature-dependent resistivity.

It is now generally accepted that this anomaly, the "Kondo effect," follows its typical temperature dependence in a region of one or more decades around the "Kondo temperature" T_K which can be defined, theoretically, as the temperature at which perturbation theory breaks down in treating the exchange interaction between the conduction-electron spin s and a localized spin S to infinite order. T_K should show experimentally as the temperature where the resistivity has a *pure* $\log_{10} T$ dependence. It has further been shown that the Kondo effect takes place in any system with magnetic moments localized on transition-metal or rare-earth atoms, contained either as dilute impurities or as components of intermetallic compounds, whenever the exchange integral J in the $\vec{s} \cdot \vec{S}$ interaction is negative.

At $T \gg T_K$ there is good agreement between calculations based on the $J\, \vec{s} \cdot \vec{S}$ exchange model and the experiments.[1] At $T \lesssim T_K$ the above theory gives only a qualitative and not a detailed agreement with the observed behavior for the temperature dependence of the resistivity as well as for the other measurable parameters.

If one considers the experimental results well below T_K, they can be described as an approach to a "nonmagnetic" state for $T \to 0$. For example, it appears that in the limit of low enough temperatures and concentrations, the resistivity obeys a law of the type $\rho(T) = \rho(0)\,[1 - (T/\theta)^2]$,[2,3] which has also been observed for systems where localized magnetic moments are not expected to be formed.[4]

These observations cast some doubt as to whether the $\vec{s} \cdot \vec{S}$ exchange model, which presupposes a well-defined and temperature-independent impurity spin, is completely valid well below T_K. On the other hand, developments based on the more complete Anderson Hamiltonian have not yet reached the stage of giving usable expressions for the observable parameters.[5]

There is also, from the experimental point of view, a lack of systems with accurate and reliable results in the range $T \sim T_K$ to compare with the theories and to point to possible improvements.

We present, in this paper, very high-accuracy resistivity measurements (up to a few ppm) on Zn alloys with Mn and Cr in the extreme dilution region (down to 0.1 ppm), and at temperatures $T \gtrless T_K$, as well as on *Zn* Fe, whose behavior is "nonmagnetic" (in the sense stated above). Preliminary results on *Zn*V and *Zn*Co are also presented, which show that these last two systems are not likely to give useful information on the present problem. A preliminary report of these measurements has already been given.[6]

In the Appendix we also give a review of all previous measurements on the Zn–transition-metal system. This system is, in our opinion, extremely valuable for a better understanding of the problem of the formation of localized magnetic moments in metals, because of the large number of different properties (e.g., superconductivity, de Hass–van Alphen effect, etc.) which have been measured.

II. SAMPLE PREPARATION AND MEASUREMENTS

A. Sample Preparation

The method of preparation was identical to that previously used by Boato *et al.*[7] Zinc-based alloys are, in principle, easy to prepare and to control, but a number of difficulties may arise, which we would like to point out.

Our alloys were prepared by mixing (at around 450 °C) pure zinc with master alloys prepared as in Ref. 7; the mixing was carried out in a Pyrex glass container under an atmosphere of pure argon. The container was then quickly evacuated to less than 1 Torr, and the molten alloy cast in a graphite- (Aquadag-) covered Pyrex tube which had been previously outgassed for $\frac{1}{2}$ h at 480 °C together with all other surfaces which were to come into contact with the molten alloy. Immediately after casting, an atmosphere of argon was readmitted, thus pushing the alloy into the casting tube, and the tube itself was quenched in water. In the case of alloys of concentrations below 20 ppm, a distinct improvement is obtained by carrying out the mixing and casting under pumped vacuum (Bell, Ref. 8; see also the data in the Appendix).

With this method, rods of 0.8–2.0 mm diameter and up to 30 cm in length were obtained, and no further strains were introduced on extracting them from the graphite-covered tube.

All the freshly prepared alloys were then controlled by measuring the residual resistance ratios

$$R_{4.2}/(R_{273} - R_{4.2}) = R_{\mathrm{ratio}} .$$

Several hundred alloys have been prepared in this way in our laboratory. If we compare the values of R_{ratio} for freshly prepared specimens with the nominal concentrations, we find that below the limits of solubility[7] the two always scale linearly. We have noted, furthermore, that samples prepared as above are always very reproducible in their resistive and also their superconducting behavior.[7] The homogeneity, tested by measuring R_{ratio} on both ends of each casting, is always better than 5%, provided that the mixing has been carried out thoroughly.

Annealing of Zn specimens must be carried out in very high-purity argon (or another inert gas), and it is advisable to keep the annealing time as short as possible. Even with these precautions, annealing often results in a sample whose behavior shows all the signs of the presence of precipitation or oxidation of the impurities, i.e., enhanced interaction effects in $\rho(T)$ and T_c, and an anomalous R_{ratio}. These samples also tend to decay more quickly in time after the annealing process.

For the above reasons we have preferred to measure fresh samples quenched directly from the melt. This was not always possible when the maximum accuracy of measurement had to be obtained. In these cases, the samples were cold drawn to about 0.3-mm-diam wires and then given a strain-relieving anneal followed by quickly cooling in a He^4 gas stream. In all these cases, however, in addition to the cold-drawn specimen, a piece of the rod quenched from the melt was also measured to allow a comparison between the absolute values of the resistivity and to check the total $\rho(T)$ variation.

Cold working must be avoided above about 20 ppm in *Zn*Cr and *Zn*Mn because it tends to give rise to enhancement of the interaction effects, even if great care is taken in the subsequent strain annealing.

The measurements of $\rho(T)$ were also used to determine the purity of the starting Zn, relative to Kondo-type impurities, whenever a new batch had to be used; only pure Zn, which did not show any minimum in $\rho(T)$ to within 10^{-6} to below 1 °K, was used. It should be noted that the requirement for the over-all purity of the starting Zn is less stringent compared to the requirement which arises in noble metals; because Fe is nonmagnetic in Zn, any small traces of Fe (which are almost unavoidable in any metal) do not give any sizable contribution to $\rho(T)$.

The concentrations of the samples above 5 ppm were obtained by comparing R_{ratio} with the linear relationship between the residual resistance ratio and the concentration obtained from the analysis of several samples within the solubility limit. Only in the case of one master alloy (*Zn*Cr) was a noticeable difference found between the values of the analysis and the nominal concentration. It must be pointed out, however, that in all cases, but especially for *Zn*Cr, it has been very difficult to obtain good and reproducible agreement between the concentration values obtained from different analytic laboratories on the same alloy. The values quoted below for R_{ratio}/c have been obtained from the analysis of the three laboratories which yielded, over several samples, results scaling linearly with the residual resistance ratio (and with the nominal concentration).[9]

Below 5 ppm, using the measurements of R_{ratio} is no longer reliable because of the random contributions to $R_{4.2}$ from other causes such as speed of quenching, size effects, cold working, etc. In these cases we have determined the value of the concentration using the known concentration of the "master" alloy (normally of ~ 10 ppm) and the dilution factor. We find that these values scale linearly with the logarithmic slope of $\rho(T)$, which confirms that they are correct.

B. Measurements

The samples were measured in a He^3 cryostat, similar to that previously used by one of us.[10] Thermal contact was ensured by "sandwiching" the samples between two copper plates, one of which was hard soldered to the He^3 can. A thin layer of silicone grease improved the contact between the samples and the plates. Electrical insulation was obtained by using thin paper impregnated with

GE7031 cement and cured at 150 °C, which covered the copper plates.

The superconducting transition in the most dilute alloys was suppressed by the field (~ 50 Oe) of a permanent ferrite magnet, which did not noticeably alter the resistivity.

Current contacts were soft soldered to reduce power dissipation, while potentiometric contacts were made with spring-loaded copper knife edges.

Preliminary measurements of the potential across the samples were made with an accuracy of 10^{-4}, by using a Keithley model No. 260-nV source to suppress over 99% of the potential, and measuring the remaining 1% or less with a Keithley model No. 148 nanovoltmeter.

The high-accuracy measurements have been performed with a different arrangement, which has been described elsewhere.[11] This allowed us to reach a relative accuracy of up to 10^{-6} and an absolute accuracy of 10^{-3} or better. The accuracy with this arrangement was limited, however, in many samples by the value of the potential drop which it was possible to establish across them, without causing any heating effects.

Temperatures were measured using two germanium resistors[12]; one, purchased calibrated between 4.2 and 40 °K, was used between 2.3 and 40 °K; the second of lower resistance, which was uncalibrated, was used between 0.3 and 3 °K.

The existent temperature calibration was checked, and the calibrations below 4.2 °K were performed, by using (i) a calibrated platinum resistor (KOL 125 from Kamerlingh Onnes Laboratorium, Leiden) above 8 °K; (ii) *Au*Fe 0.03% thermocouples to interpolate between 4.2 and 8 °K; (iii) the vapor pressures of He^3 and He^4, respectively, from 0.8 to 3.2 °K and from 1.5 to 4.2 °K; and (iv) a ruby susceptibility thermometer between 0.3 and 1.2 °K. The accuracy of the temperature calibration is within 5 m °K below 1 °K and better than 0.5% above 1 °K.

III. RESULTS AND DISCUSSION

The values of $(\Delta\rho/c)_{4.2^\circ\mathrm{K}}$ in $\mu\Omega$ cm/at.% ($\Delta\rho = \rho_{\mathrm{alloy}} - \rho_{\mathrm{pure\ Zn}}$) have been calculated, assuming that Matthiessen's rule is valid at room temperature, by multiplying the slope of the observed linear variation of R_{ratio} with the analyzed concentrations by the resistivity of pure Zn at 273 °K ($\rho_{273} = 5.5\ \mu\Omega$ cm); i.e.,

$$\left(\frac{\Delta\rho}{c}\right)_{4.2^\circ\mathrm{K}} = \frac{R_{\mathrm{ratio}}(\mathrm{alloy}) - R_{\mathrm{ratio}}(\mathrm{pure})}{c}\ \rho_{273}(\mathrm{pure}) \ .$$

These values are $(\Delta\rho/c)_{4.2^\circ\mathrm{K}} = 17.5 \pm 2\ \mu\Omega$ cm/at.% for *Zn*Cr, $19.0 \pm 0.6\ \mu\Omega$ cm/at.% for *Zn*Mn, and $15.4 \pm 0.3\ \mu\Omega$ cm/at.% for *Zn*Fe, and are shown in Fig. 1 together with previous measurements. The values for $(\Delta\rho/c)_{0^\circ\mathrm{K}}$ will be discussed later in this section. We must note that in the case of *Zn*Cr and *Zn*Mn the values at 4.2 °K are different from the zero-temperature values which define the residual resistivity.

Two sets of measurements were performed on the *Zn*Cr alloys: The first one, of lower accuracy, was intended to observe the general behavior of $\rho(T)$ for *Zn*Cr as a function of concentration, which was previously unknown, and to select the best concentration interval for more accurate measurements. This set is shown in Fig. 2 in a $\log_{10}T$ plot; the ordinates have been scaled to have the $\rho(T)$ behavior almost parallel; for $c > 40$ ppm we observe a concentration-dependent curvature due to interactions between impurities.

In Fig. 3 we show the slope of the "pure" $\log_{10}T$ part of the curve, observed between 1 and 2 °K, as a function of concentration. We observe that the slope is not concentration independent, but changes rather suddenly by a factor ~ 2 between 20 and 40 ppm; we observe, furthermore, that below and above this value of concentration the behavior of the logarithmic slope is linear in c. This behavior has been found to be due to a partial oxidation of the Cr content, probably due to oxygen impurities contained in the argon (about 15–20 ppm) (see also sample preparation).

This effect is changing our concentrations but not the temperature dependence: Our concentrations for *Zn*Cr might therefore be in error by a factor of 2 below 20 ppm. No other concentration effects have been found in either *Zn*Cr or *Zn*Mn below about 20 ppm; we therefore considered this

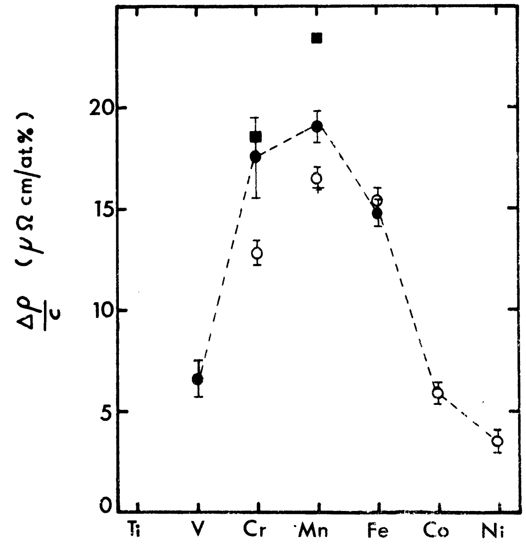

FIG. 1. $\Delta\rho/c$ ($\mu\Omega$ cm/at.%) for the *Zn*–3*d*-transition series. Measurements at 4.2 °K: ●, present measurements; ○, Ref. 7; ■, calculated values at 0 °K for *Zn*Cr and *Zn*Mn.

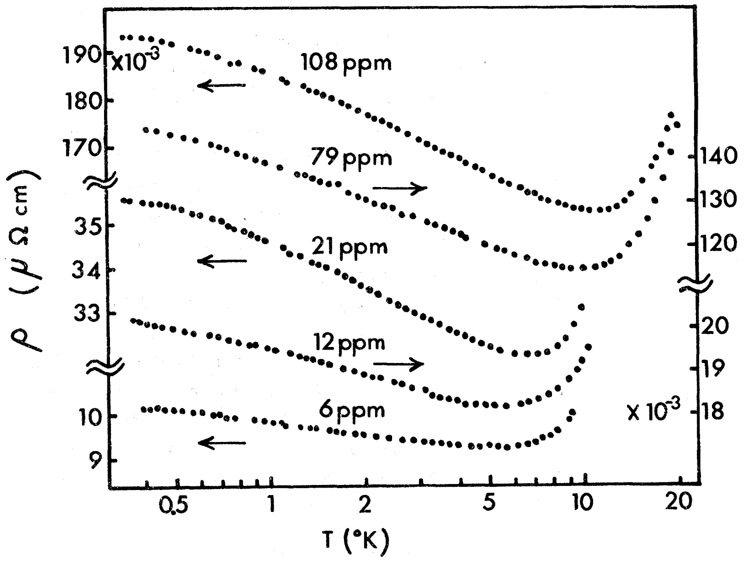

FIG. 2. ρ ($\mu\Omega$ cm) vs $\log_{10}T$ for ZnCr alloys.

concentration as the upper limit of the dilute range, and have confined our more accurate measurements to below this value.

The resistivity measurements on some of the dilute samples are reported as a function of $\log_{10}T$ in Figs. 4–6 for ZnCr, ZnMn, and ZnFe, respectively. In all these alloys, we have corrected for the resistivity contributions due to the pure zinc and the metallurgy of the specimens by subtracting the difference between the measured $\rho(4.2)$ and the $\rho(4.2)$ expected from the nominal concentration for each alloy from all the experimental points. The above contributions to $\rho(4.2)$ varied between 5.5×10^{-9} and 16×10^{-9} Ω cm depending on the degree of cold working. We observe in Figs. 4 and 5 that both ZnCr and ZnMn have a $\log_{10}T$ dependence, indicative of a Kondo effect, but also that both systems show a *concentration-independent* "bending" from a $\log_{10}T$ behavior. This happens below about 0.6 °K for ZnCr and, with less certainty since it was only observed on two alloys, below about 0.5 °K for ZnMn. These results, by comparison with other systems,[1] suggest that for both alloys T_K is higher than the "bending point," and that its value is probably above 1 °K in both cases. The actual distance between T_K and the "bending point" should depend, according to the qualitatively valid predictions of Hamann's[13] theory, on the value of the impurity spin S. In addition, the rather large value of the logarithmic derivative of resistivity versus temperature which we observe would suggest that T_K is in our temperature interval; in fact, our observed values are 1.66 and 2.8 $\mu\Omega$ cm/at.% per decade for ZnCr and ZnMn, respectively, while previous observed values are 8.0, 1.3, 0.8, 0.15, 0.12, respectively, for CuCr,[14] AuFe,[3] CuMn,[15] AgMn,[16] and AuMn,[17] whose Kondo temperatures were given equal to 1.2 °K,[18] 0.24 °K,[3] 2 m °K,[19] < 0.1 °K,[20] and $\ll 10^{-6}$ °K,[17] respectively.

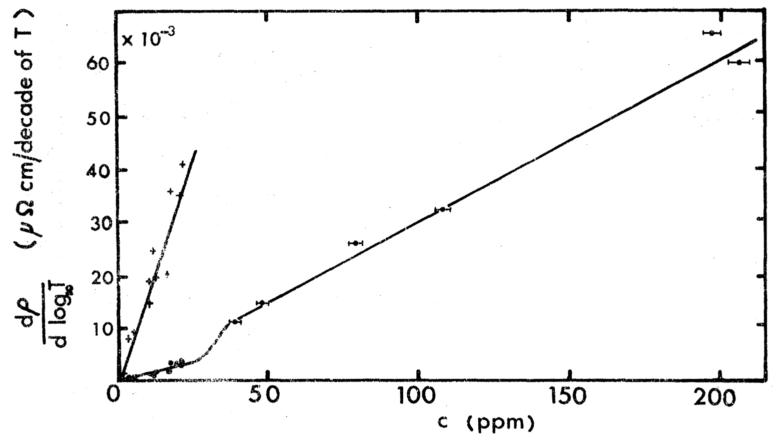

FIG. 3. Logarithmic slope of the resistivity for ZnCr alloys, measured between 1 and 2 °K ($\mu\Omega$ cm/decade of T), vs concentration (ppm). ●, measured values; +, scale expanded by a factor of 10 for the dilute alloys.

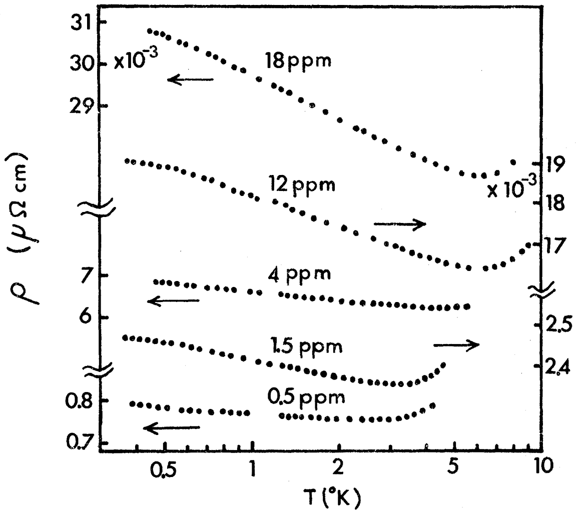

FIG. 4. ρ ($\mu\Omega$ cm) vs $\log_{10}T$ for very dilute ZnCr alloys, high-accuracy measurements.

In Fig. 7 we plot the resistivity against T^2 for some of the ZnCr and ZnMn alloys, and in Fig. 8 for the ZnFe alloys. From Fig. 7 it can be seen that both ZnCr and ZnMn tend to approach a T^2 temperature dependence in the small temperature interval where a pure $\log_{10}T$ dependence is no longer followed. This observation, which we have already reported,[6] has been found to hold for other systems.[2,3]

Let us now briefly consider the behavior of ZnFe in Figs. 6 and 8. Our measurements are in good agreement with Caplin's[21] results in the 1.5–4.2 °K range for the sample with a concentration of 231 ppm, which is the same specimen as he measured. We observe, however, that extending the measurements over a wider temperature interval it is no longer possible to fit the behavior of $\rho(T)$ to a $\log_{10}T$ dependence, but rather that it also follows a T^2 temperature dependence. These measurements will be discussed more fully later in this paper.

We will first discuss our data on ZnCr and ZnMn and try to compare them quantitatively with some theoretical results. We compare our data with Hamann's[13] expression which is thought to be one of the most valid across T_K. This expression, which is obtained from the $\vec{s}\cdot\vec{S}$ model, is

$$\rho(T)=A+\frac{R_0}{2}\left(1-\frac{\ln(T/T_K)}{[\ln^2 T/T_K+\pi^2 S(S+1)]^{1/2}}\right), \qquad (1)$$

where R_0 is the s-wave unitarity limit, S the impurity spin, and A is the value of the resistivity when the "Kondo" contribution is zero, i.e., at $T=\infty$.

It has already been shown[1,3] that Eq. (1) reproduces all the important features of the experimentally observed behavior over large temperature intervals. Improvements in this equation have been suggested by several authors who have derived it by other methods.[22–25] Its functional dependence on T is also found to be preserved by including the effect of potential scattering.

We will use Eq. (1), which is the simplest, avoiding for the moment the strong complications introduced in the other formulas obtained by more complete treatments.

In comparing the data with Eq. (1) we can use two different approaches:

(i) Fit our data to Eq. (1) leaving all the parameters free, and extract S, T_K, and also the slope $B=\frac{1}{2}R_0$. We adopted this approach in our earlier communication[6] on the preliminary data on fewer samples and we found the following values: For ZnCr

$A\sim 14.5\pm 1$ $\mu\Omega$ cm/at.%,

$B\sim 3.6\pm 0.5$ $\mu\Omega$ cm/at.%,

$S\sim 0.6$, and $T_K\sim 2$ °K.

For ZnMn

$A\sim 12\pm 2$ $\mu\Omega$ cm/at.%,

$B\sim 4\pm 1$ $\mu\Omega$ cm/at.%,

$S\sim 1$, and $T_K\sim 1$ °K.

With the above values, the experimental data were reproduced to better than $1/10^3$.

(ii) Try to "fix" some of the parameters using values from other published data. We have already shown,[6] however, that for ZnMn if both S and T_K are derived from low-temperature susceptibility measurements,[26] then the accuracy of the

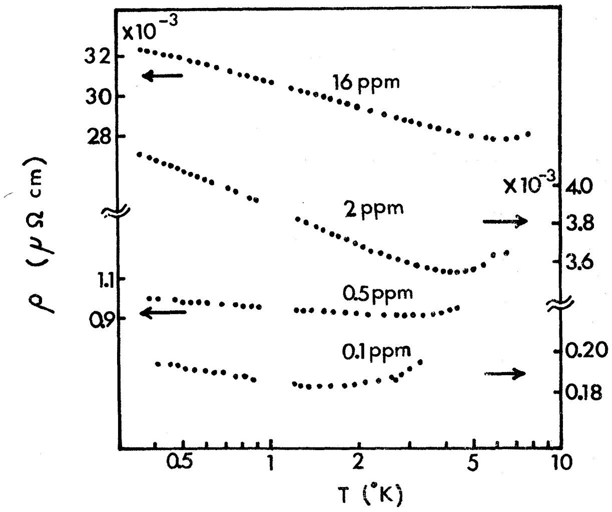

FIG. 5. ρ ($\mu\Omega$ cm) vs $\log_{10}T$ for very dilute ZnMn alloys, high-accuracy measurements.

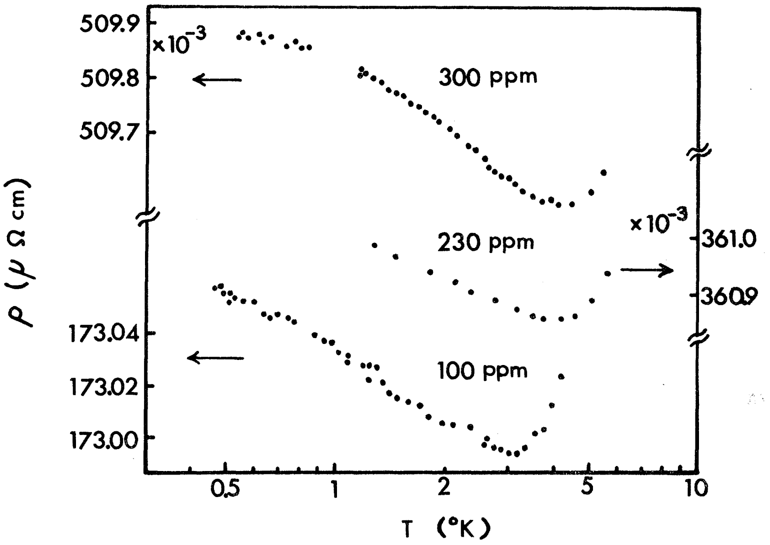

FIG. 6. ρ ($\mu\Omega$ cm) vs $\log_{10}T$ for *Zn*Fe alloys.

fit decreases by an order of magnitude. Instead we choose spin values obtained from high-temperature susceptibility measurements and see how this influences the accuracy of the fitting and the values of the other parameters. This choice is justified because the theory is supposed to be valid with a constant spin value equal to the value obtained from high-temperature susceptibility measurements and this is a point we wished to test.

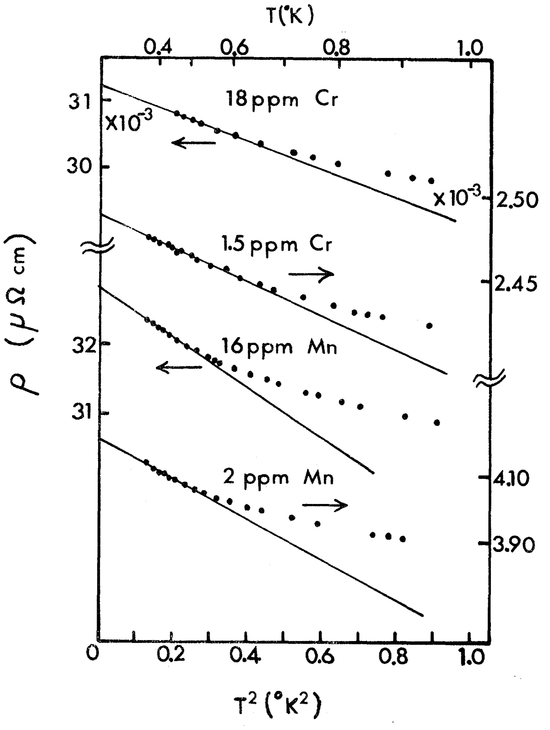

FIG. 7. ρ ($\mu\Omega$ cm) vs T^2 (°K^2) for very dilute alloys of *Zn*Cr and *Zn*Mn.

Unfortunately direct values of S for *Zn*Cr were not available to us and so the spin values used are $S=1$ for *Zn*Cr[10] and $S=\frac{3}{2}$ for[27] *Zn*Mn (see Appendix). The fitting procedure was similar to that described by Loram *et al.*[3] For both alloys we are again able to reproduce the experimental results to better than $1/10^3$ with the following parameters: For *Zn*Cr

$$A=12.4\pm1.5\ \mu\Omega\,\mathrm{cm/at.\%}\,,$$

$$\tfrac{1}{2}R_0=B=3.4\pm0.5\ \mu\Omega\,\mathrm{cm/at.\%}\,,$$

$$T_K=3\,°\mathrm{K}\,.$$

For *Zn*Mn

$$A=11.5\pm1.0\ \mu\Omega\,\mathrm{cm/at.\%}\,,$$

$$\tfrac{1}{2}R_0=B=6.1\pm0.5\ \mu\Omega\,\mathrm{cm/at.\%}\,,$$

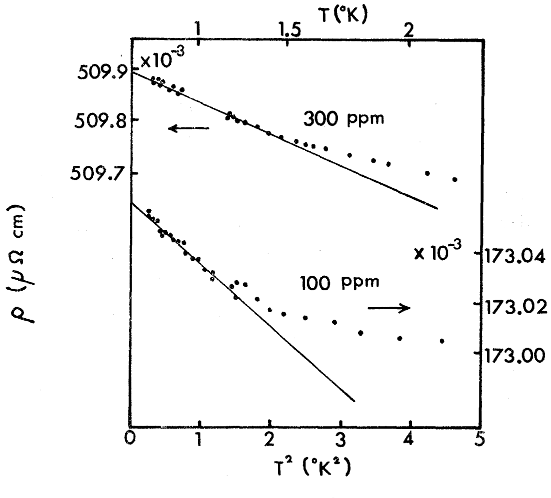

FIG. 8. ρ ($\mu\Omega$ cm) vs T^2 (°K^2) for *Zn*Fe alloys.

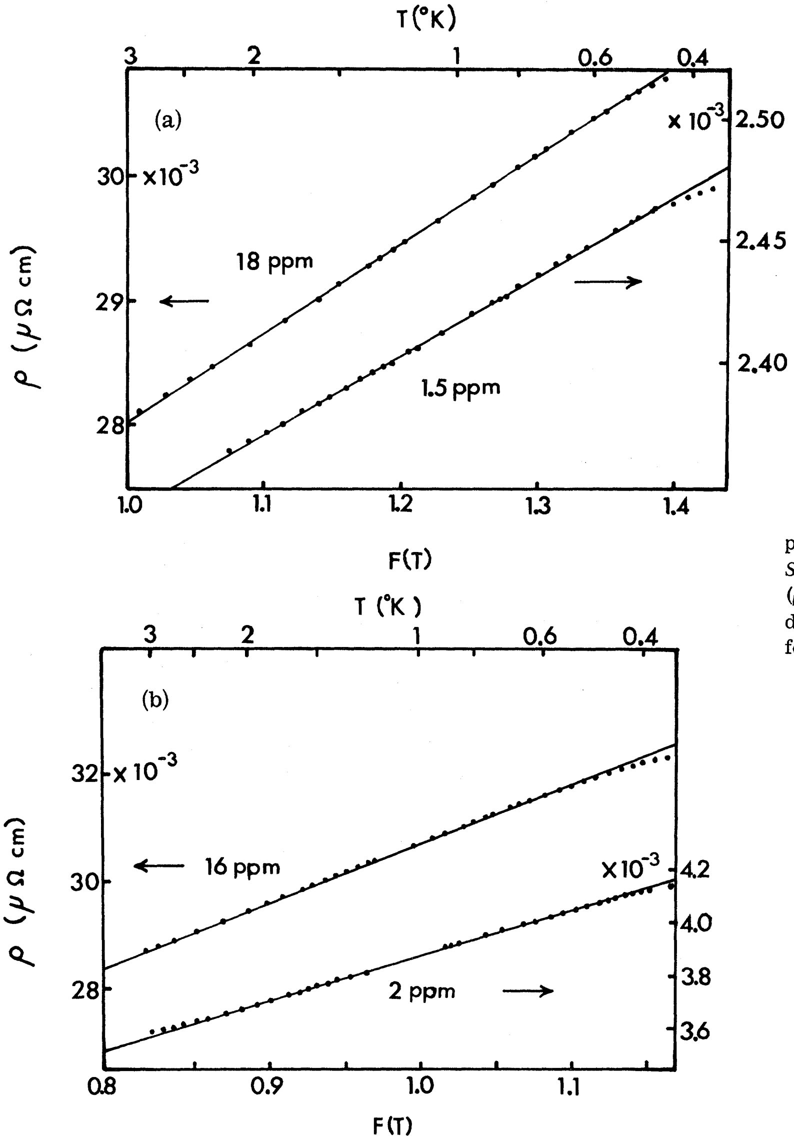

FIG. 9. (a) ρ ($\mu\Omega$ cm) vs $F(T)$, the temperature-dependent part of Eq. (1), using $S=1$, $T_K=3$, for *Zn*Cr alloys. (b) ρ ($\mu\Omega$ cm) vs $F(T)$, the temperature-dependent part of Eq. (1), using $S=\frac{3}{2}$, $T_K=1$, for *Zn*Mn alloys.

$T_K = 1\,°\mathrm{K}$.

The fit to Eq. (1) with the above parameters for some of the *Zn*Cr and *Zn*Mn alloys is shown in Fig. 9. The possibility of obtaining equally good fits by using values of T_K and S very different from those used above was checked and found not to be the case. On the other hand, if the values of T_K and S are varied by sensible amounts around the values given above, we still obtain similar values of B.

In Figs. 10 and 11 we show the values of $\frac{1}{2}R_0$ derived for all the alloys measured using the values of T_K and S indicated above. We see that the linear relationship with concentration is good and this suggests that the values obtained are accurate.

If, in Fig. 9, we compare the theoretical curves obtained using the values of B, T_K, and S quoted above with the experimental curve we note that there is a systematic deviation between the two at low temperatures. This could be reduced by allowing the S value to decrease with T, as has already been noted,[28] and is suggested by the lower S value obtained in the first fitting procedure. We note, on the other hand, comparing Figs. 9 and 7, that a T^2 behavior seems to be approached when deviations from Eq. (1) become appreciable.

According to Caplin and Rizzuto[4] and Rivier and Zuckermann,[29] the resistivity arising from localized spin fluctuations (LSF) is given by

$$\rho(T)=\rho(0)\left[1-(T/\theta)^2\right] , \tag{2}$$

where θ is a characteristic spin-fluctuation temperature. The physical relationship between θ and T_K is still not clear. In Fig. 7 we observe that the

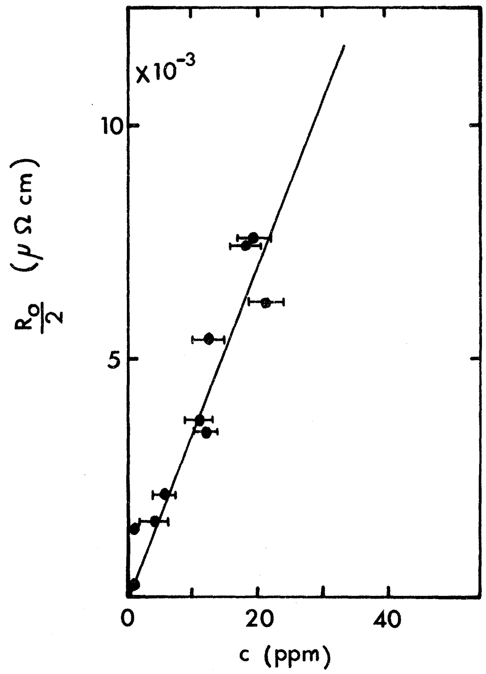

FIG. 10. $\frac{1}{2}R_0$ ($\mu\Omega$ cm), defined as in Eq. (1), vs concentration (ppm) for dilute *Zn*Cr alloys.

T^2 dependence starts below about 0.6 °K for *Zn*Cr and 0.5 °K for *Zn*Mn. The temperature region where this is observed is very narrow, but this observation is supported by what has already been found in other systems.[2,3] The characteristic temperatures obtained by extrapolation of the T^2 term are approximately (4.5 ± 0.5) °K for *Zn*Cr and (2.5 ± 0.5) °K for *Zn*Mn, which are comparable but larger than the T_K values obtained from Eq. (1). (Recent measurements down to 50m °K,[30] although confirming the deviation away from a pure $\log_{10}T$ behavior, indicate that the T^2 region had not yet been reached in our measurements, and imply lower characteristic temperatures.)

We will now discuss in more detail the behavior of *Zn*Fe. It has already been observed that the alloys follow a T^2 temperature dependence up to 1.5 °K and that at higher temperatures the resistivity tends to a $\log_{10}T$ dependence when a gross subtraction is made for the phonon resistivity. Applying Eq. (2) to the T^2 temperature region yields a characteristic temperature θ of (85 ± 10) °K. Using this value of θ, we attempted to fit our data to Eq. (1) using trial spin values of 1, 0.1, and 0.01. (The earlier resistivity work of Caplin[21] implied $p_{\rm eff}^2 = 0.07$ corresponding to $S \sim 0.02$.) It was found that only a very rough fit of the data to Eq. (1) was possible, and that the accuracy of the fit did not depend on the value of the spin chosen. A value of B of 0.07 ± 0.02 $\mu\Omega$ cm/at.%, which was independent of S, was obtained, and this is substantially smaller than that found for *Zn*Cr or *Zn*Mn. This difficulty in fitting our data is probably not surprising in view of the fact that we are comparing it to Hamann's[13] equation at temperatures well below T_K. If we now compare both the resistivity and the superconductivity behavior of *Zn*Fe (see Appendix) with that of *Al*Mn, *Al*Cr,[10] and *Th*U [31] we see that they are similar and that the last three systems have all been considered as examples of LSF: It seems reasonable, therefore, to also consider *Zn*Fe from the same standpoint. On the other hand, we should note that while for *Zn*Cr and *Zn*Mn, and also for *Al*Mn, *Al*Cr,[32] and *Th*U,[31] the T^2 term in $\rho(T)$ is observed to more than 0.1θ, instead, for *Zn*Fe, we can only observe the T^2 term to 0.02θ. This different behavior may be due to a phonon contribution although it is observed at very low temperatures. An alternative possibility may be that the observed effects are due to a small percentage (~ 10%) of the Fe atoms being paired or clustered with a substantially lower characteristic temperature. Some support for this possibility comes from some recent measurements[33] on rapidly quenched *Zn*Fe alloys, where a T^2 dependence of the resistivity has possibly been observed up to about 5 °K. Caplin[21] also noted that the behavior of Fe impurities in zinc seemed very sensitive to metallurgical treatment.

Preliminary resistivity measurements were also made on *Zn*V and *Zn*Co alloys. In both systems

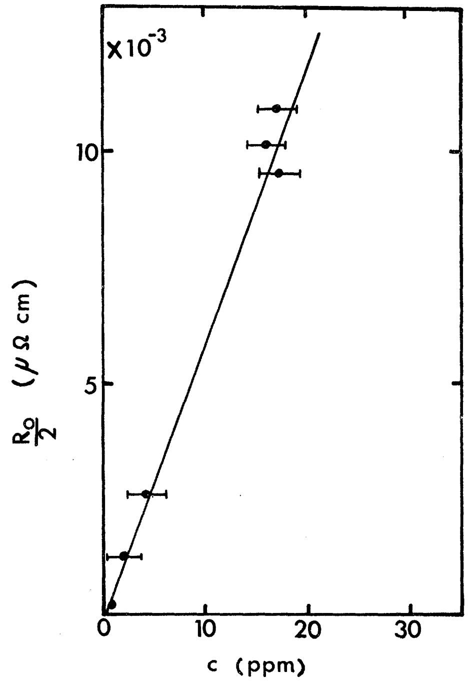

FIG. 11. $\frac{1}{2}R_0$ ($\mu\Omega$ cm), defined as in Eq. (1), vs concentration (ppm) for dilute *Zn*Mn alloys.

there was considerable difficulty in getting the impurities into solution. In Fig. 1 we give the possible values of $\Delta\rho/c$. With both systems very weak resistance minima were observed on several samples. However, these minima varied randomly with the Co and V concentration and were attributed to traces of manganese or chromium. We have concluded therefore, that *Zn*V and *Zn*Co are both nonmagnetic, or have a very high θ ($\theta > 1000\,^\circ$K).

Using the values of B obtained for *Zn*Mn and *Zn*Cr, and the values of $(\Delta\rho/c)_{4.2^\circ\mathrm{K}}$, we have evaluated the residual resistivity of the Zn-transition-metal system at $T = 0\,^\circ$K, $(\Delta\rho/c)_{0^\circ\mathrm{K}}$, from *Zn*V to *Zn*Ni. For *Zn*Fe the resistivity at 0 °K is practically unchanged, compared with the value at 4.2 °K, and we have assumed no variation in the case of *Zn*V, *Zn*Co, and *Zn*Ni. These values are tabulated in Table I. In obtaining these values we have subtracted a contribution of 0.6 $\mu\Omega$ cm/at.%, which is the resistivity arising from nonmagnetic scattering obtained from existing measurements on a *Zn*Cu alloy.[7] We can now compare these values with those calculated from the Friedel model[7,34] assuming d-wave scattering and nonmagnetic virtual bound state

$$\frac{\rho_d}{c} = \frac{h}{10 Z_h e^2 k_F} \sin^2 \frac{\pi Z_d}{10}\,, \tag{3}$$

where Z_h is the number of valence electrons in the host metal and Z_d the number of d electrons localized near the transition-metal impurity. To reproduce our experimental results (i.e., that the impurity resistivity at 0 °K peaks around manganese), we have chosen $Z_d = 2, 4, 5, 7, 8, 9$ for V, Cr, Mn, Fe, Co, and Ni, respectively. In Table I we show the impurity resistivity calculated in this manner. We observe that there is an approximately constant ratio between the experimental and the calculated values of the resistivity $\alpha = 2.5 \pm 0.4$, which is equal to that found earlier.[7] This difference arises from the use of the free-electron model which assumes that the number of conduction electrons provided by each zinc atom, n_{eff}, is 2. Farrell *et al.*[35] have examined the residual resistivity of zinc containing nonmagnetic impurities and have discussed the results in terms of Blatt's[36] model for impurity resistivity. n_{eff} was difficult to calculate and was treated as a parameter which was obtained from the experimental data. n_{eff} was found to be 0.6, which is just under one-third of the available conduction electrons and this, therefore, implies that significant screening is taking place. Our own data give $n_{\mathrm{eff}} = 0.8 \pm 0.1$ and suggest that a similar analysis to that of Farrell *et al.*[35] is possible for transition-metal impurities.

TABLE I. Residual resistivity of Zn–3d-transition-metal series. α is the ratio between the experimental and theoretical values.

	Z_d	$\left(\frac{\rho_d}{c}\right)_{\mathrm{expt}}$	$\left(\frac{\rho_d}{c}\right)_{\mathrm{theor}}$	α
*Zn*V	2	6.5 ± 1.0	2.84	2.29
*Zn*Cr	4	19.0 ± 1.0	7.45	2.5
*Zn*Mn	5	23.5 ± 1.0	8.24	2.85
*Zn*Fe	7	14.8 ± 0.3	5.38	2.75
*Zn*Co	8	6.2 ± 0.3	2.84	2.18
*Zn*Ni	9	1.9 ± 0.3	0.78	2.44

One interesting feature of the results is the strong similarity between the magnetic state of chromium and manganese in zinc as shown by their very similar Kondo temperatures. This can be compared with the behavior of these impurities in the noble metals. Estimates of the Kondo temperature of *Cu*Mn[19] and *Cu*Cr[18] show that these differ by nearly three orders of magnitude and although the Kondo temperatures of *Au*Mn[17] and *Au*Cr[20] are not so well established, the data again suggest that they probably differ by at least the same amount. Rather surprisingly, the only estimate of the Kondo temperature of *Ag*Mn and *Ag*Cr[20] suggest that the former is slightly higher. However, this result has been obtained using the nuclear orientation technique and the interpretation of the data has recently been queried.[19]

A difference between zinc and the noble metals is that the former is a hcp metal, whereas the latter are all fcc, and this difference in host structure may be playing an important role. Recently, Hirst[37] has drawn attention to the importance of considering the orbital angular momentum of 3d impurities in metals, showing that in host metals with high symmetries this is not necessarily quenched and can give rise to rather complicated effects because the spin and the orbital moments are dynamically coupled by the spin-orbit interaction. He also reports that some of the strongest effects of an unquenched orbital angular momentum are to be expected from a 3d impurity in a hcp metal such as zinc. Hirst[37] has thus been able to qualitatively account for a reduction in the Kondo temperature of zinc containing chromium impurities, although no estimates have been made of the magnitude of the reduction.

IV. CONCLUSIONS

We have studied the electrical resistivity of a number of alloys of zinc containing impurities of the first-row transition metals down to 0.35 °K. We wished to check in what temperature range these systems could be interpreted in terms of either the $\vec{s}\cdot\vec{S}$ exchange model or the LSF model. Previous resistivity data on *Zn*Mn (see the Appendix) indicated a Kondo temperature of 1 °K and this means that this system is one of the very few where it is possible to study the experimental behavior around and below T_K, where theory is very uncertain. We found that we could accurately fit Hamann's[13] equation to our data using $S=1$, $T_K=3$ for *Zn*Cr and $S=\frac{3}{2}$, $T_K=1$ for *Zn*Mn. Below about 0.6 °K for *Zn*Cr and 0.5 °K for *Zn*Mn we find that this formula is no longer a good fit and both systems appear to follow a T^2 dependence, as predicted by LSF theory, with characteristic temperatures θ of (4.5 ± 0.5) °K for *Zn*Cr and (2.5 ± 0.5) °K for *Zn*Mn. These characteristic temperatures are comparable to the T_K values obtained using the $\vec{s}\cdot\vec{S}$ exchange model and this supports an equivalence between the LSF and the Kondo characteristic temperatures as has been found for other systems.[2] This implies, for these systems, either an equivalence between the LSF and $\vec{s}\cdot\vec{S}$ approaches at $T\ll T_K$, as suggested theoretically,[29] or the coexistence of both LSF and Kondo effect on the same impurity site, the former being predominant at low temperatures and having, in this case, characteristic parameters comparable to the latter.

In the second hypothesis, the equivalence between θ and T_K would imply that all the alloys considered are very near to the magnetic to nonmagnetic transition, although it is not possible to decide on which side they are. This viewpoint is supported by the observation that the resistivities at 4.2 and 0 °K are very nearly equal and can be interpreted as due to a nonmagnetic virtual bound state.[7,34]

We also note that recent high-temperature resistivity measurements on[38] *Al*Mn suggest that a logarithmic T dependence in $\rho(T)$ (Kondo effect) is not necessarily observed for any alloy which shows LSF effects, in agreement with recent theoretical work by Dworin.[39]

For *Zn*Cr and *Zn*Mn the T^2 temperature dependence was observed below about 0.2θ, which is comparable to observations in other systems. In contrast, the observation of a T^2 temperature dependence up to only 0.02θ in *Zn*Fe suggests that in this alloy system clustering effects influence the observed behavior.

The values of T_K for *Zn*Cr and *Zn*Mn obtained in this work are very close, compared to the noble-metal alloys, possibly due to the different crystal field symmetry of this hcp metal.

It can be seen from the Appendix that only *Zn*Mn has been studied extensively by a wide variety of techniques, whereas substantially less is known about *Zn*Cr and *Zn*Fe. An extension of resistivity and susceptibility measurements to below 0.1 °K for *Zn*Mn and *Zn*Cr will be useful to clear up some of the uncertainties of the measurements. Further measurements on *Zn*Fe, after understanding its metallurgical complications, are also needed.

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APPENDIX: REVIEW OF PUBLISHED DATA

It is well known that in studying the "Kondo effect" in each alloy system a detailed knowledge is necessary of several different impurity-dependent parameters measured over the widest possible temperature range in order to obtain a reasonable comparison with the possible theories. We will, therefore, briefly review and comment on all previous published data on the systems which we have considered. Most of these data have been obtained on alloys which were too concentrated to give results which were free from effects due to interactions between impurities. Taking this fact into account, however, it is still possible to extract information relating to the main problem, i.e., the study of interactions between electrons and a single isolated impurity.

All the information concerning the type of measurements and the explored ranges of temperatures, concentrations, and magnetic fields, together with the reference numbers, are summarized in Table II.

ZnMn System

This system has been investigated extensively. *Resistivity* measurements clearly show a "Kondo effect."[40-45] In all references, however, concentration-dependent effects appear above a concentration of 20 ppm: This suggests that long-range interactions between the impurities appear above this concentration, at temperatures $T\sim 50$ °K/at.%. These interactions, unlike most other systems, do not give rise to a well-defined maximum, unless $c>0.2$ at.% ($T_{\max}\sim 3$ °K)[41]: This was interpreted[41] as due to the coexistence of RKY-type interactions and spin compensation, with an estimated Kondo temperature of about 2 °K. The interaction effects above 20 ppm are clearly enhanced when dealing with inhomogeneous or partially reprecipitated alloys.[43,45]

Measurements have been made by Newrock *et al.*[26] on very dilute alloys (7.8–38 ppm) down to 0.1 °K. The alloys were measured using the ac eddy-current technique with an accuracy of 1 in 10^3 at 0.5 °K. They showed very clearly that concentration effects persist down to 12.1 ppm. A 7.8-ppm Mn specimen, however, showed no evidence of interactions and followed a $\log_{10}T$ dependence down to the lowest temperature of measurement. This is in contrast to our measurements where we observe a concentration-independent bending from a $\log_{10}T$ dependence below 0.5 °K. Measurements down to 0.05 °K [30] on our specimens again show clear evidence of a departure from a pure $\log_{10}T$ behavior below 0.5 °K.

Finally, the resistivity of a 64-ppm *Zn*Mn crystal has been measured both parallel and perpendicular to the *c* axis.[46] The difference in the temperature dependence along the two orientations indicated that there was an anisotropy of the *s*-*d* exchange constant *J* of several percent.

a. Susceptibility measurements. These have been made in the temperature and concentration ranges 4–300 °K and 0.04–0.4 at.%, giving a value of $S=\frac{3}{2}$ for the localized spin at high temperature.[27] Other measurements[26] between 1 and 4 °K and 7.6 and 182.2 ppm give $p_{\text{eff}}=4.66$ ($S\sim 2$) and yield $T_K = 0.2$ °K when interpreted using perturbation theory. We must note, however, that the observed concentration-independent negative Curie temperature was 0.8 °K.

b. Thermopower measurements. These measurements between 4 and 100 °K and 0.015 and 0.037 at.%,[40] and also between 0.4 and 8 °K for a 12-ppm specimen,[44] show the existence of a "giant" negative thermopower, typically due to localized moments, which has a sharp decrease below 1 °K.

c. Superconductivity measurements. In the ranges 0.3–0.85 °K and 3–14 ppm these measurements give what is probably the highest observed rate of suppression of the superconducting critical temperature by magnetic impurities, $-dT_c/dc = 315$ °K at.%,[10] which has been confirmed also by other authors.[42,47] This fact, compared with the values of $-dT_c/dc$ for *Zn*Cr, *Zn*Fe, and *ZnAl*Mn has been interpreted as evidence for T_K (*Zn*Mn) $\approx T_{c0}$ (pure Zn).[48]

d. Specific heat. An early investigation[49] on a 0.07-at.% sample between 1.4 and 30 °K indicated a spin of $\frac{3}{2}$. A much more thorough investigation was made between 0.4 and 30 °K on alloys with concentrations of 0.05 and 0.1 at.% and on a 0.2-at.% specimen up to 3 °K.[42] These measurements also gave a spin value of $\frac{3}{2}$. The 0.2- and 0.1-at.% alloys showed a concentration-independent linear specific heat at low temperatures. In a further investigation,[50] 0.02- and 0.05-at.% alloys were measured between 0.4 and 3 °K and a 0.2-at.% alloy up to 5 °K. These measurements confirmed that the temperature of the specific-heat maximum increased linearly with the concentration. No evidence was found for a concentration-independent maximum in the specific heat as would be expected for a Kondo system.

e. de Haas–van Alphen effect. This was first examined in *Zn*Mn on an 80-ppm specimen in magnetic fields up to 8 °KOe and between 1.6 and 4.2 °K. An anomaly was found in the field and temperature dependence of the amplitude of the oscillations[40] which was later accounted for[51] by considering the energy-dependent relaxation time for Kondo scattering. In later work it was found that the collision parameter scaled logarithmically with temperature,[52] which could be explained by considering a temperature-dependent relaxation time. Recently, the de Haas–van Alphen (dHvA) effect has been reexamined in a 64-ppm *Zn*Mn crystal for applied fields of 3–10 kG.[53] A weak magnetic field dependence was observed in the collision parameter and this could be understood by taking into account the effect of the applied field, which freezes out the spin degree of freedom. This would also explain the crossover of the dHvA amplitude at a finite field value observed previously.[54]

f. Nuclear orientation. This technique has recently been applied to *Zn*Mn alloys with concentrations less than 1-ppm Mn and in the temperature range 10–50 m °K.[55] It was observed that between 10 and 20 m °K, the spins no longer behaved as free but rather could be described as obeying a Curie-Weiss behavior, with an estimated θ of 0.26 °K.

ZnCr System

Investigations on this system have been much less detailed as is apparent from Table II; measurements on *resistivity* between 1.3 and 4.2 °K and 0.01 and 0.1-at.% specimens showed a resistance minimum.[56] A less concentrated sample containing 20 ppm with possibly some reprecipitation was also measured between 0.4 and 8 °K [44] giving a $\log_{10}T$ behavior. No other detailed resistivity measurements at different concentrations are available.

Preliminary *susceptibility* measurements[8] on some of the samples used in this resistivity study suggest that the spin value of *Zn*Cr is about 1.3.

The thermoelectric power was also measured[44] between 0.8 and 8 °K on the 20-ppm sample used for resistivity measurements giving results similar to those for *Zn*Mn, but without any sudden fall of the TEP value similar to that which was observed for *Zn*Mn below 1 °K.

a. Superconductivity measurements. Between 0.3 and 0.85 °K and 6 and 13 ppm, these measure-

TABLE II. Concentration, temperature, and magnetic field intervals in which the various parameters have been measured in *Zn*Mn, *Zn*Cr, and *Zn*Fe.

	*Zn*Mn			*Zn*Cr			*Zn*Fe		
Parameter	Concentration range	Temperature range (°K)	Ref.	Concentration range	Temperature range (°K)	Ref.	Concentration range	Temperature range (°K)	Ref.
Resistivity	0.006–0.42 at.%	1.6–80	40	0.01–0.1 at.%	1.4–4.2	56	28–1.000 ppm	1.5–4.2	21
	0.0058–0.332 at.%	0.4–30	41	20 ppm	0.4–8	44			
	0.05–0.2 at.%	0.4–30	42						
	0.0007 at.%	0.4–8	42						
	0.006–0.6 at.%	0.4–40	43						
	7.8–38 ppm	0.1–4.2	26						
	12 ppm	0.4–8	44						
	20 ppm	0.4–60	45						
Susceptibility (T)	0.042–0.43 at.%	4–273	27	10–200 ppm	1.3–20	8	0.1 at.%	4.2–295	58
	7.6–182 ppm	1.4–4.2	26						
Thermopower $S(T)$	0.015–0.37 at.%	4.2–100	40	20 ppm	0.4–8	44			
	12 ppm	0.4–8	44						
Superconductivity dT_c/dc	3–14 ppm	0.3–0.85	10	6–13 ppm	0.3–0.85	10	20–300 ppm	0.3–0.85	10
	7 ppm	0.3–0.85	42						
	12–24 ppm	0.3–0.85	47						
Specific heat $C(T)$	0.07 at.%	1.4–30	49	0.3 at.%	1.4–30	49			
	0.05–0.1 at.%	0.4–30	42						
	0.2 at.%	0.4–3	42						
	0.02–0.05 at.%	0.4–3	50						
	0.2 at.%	0.4–5	50						
dHvA	0.008 at.%	1.6–4.2 (0–8)	40						
(Magnetic field range in kOe in parenthesis)	0.005 at.%	1–4.2 (0–10)	52						
	0.0092, 0.0018 at.%	1.1–4.2 (0–50)	54						
	0.0064 at.%	1.1–4.2 (3–10)	53						
Nuclearorientation	<1 ppm	0.01–0.05	55						

ments give a suppression rate of T_c, $-dT_c/dc = 170$ °K at.%,[10] which is comparable to that observed in *Zn*Mn. This was interpreted, using the theory of Abrikosov and Gorkov,[57] by assuming a spin value of 1 for *Zn*Cr.

b. Specific heat. These measurements on a 0.2-at.% (nominal concentration) sample were also reported,[19] giving $S=0.3$, but this concentration is considerably in excess of the solubility limit[7] and these measurements must therefore be considered to be unreliable.

ZnFe System

Accurate resistivity measurements in the range 1.5–4.2 °K on alloys between 28 and 1000 ppm[20] showed a very small temperature-dependent term, which follows a $\log_{10}T$ behavior in this narrow range. The over-all variation of ρ in this interval was 0.015% for a 230-ppm specimen, which is about 1000 times smaller than that observed in *Zn*Mn and *Zn*Cr of comparable concentration.

Only preliminary but inconclusive measurements of *susceptibility* are known[58] and there appears to be no published data on the *thermoelectric power.*

The suppression of superconductivity in *Zn*Fe was studied in samples with concentrations between 20 and 300 ppm and between 0.3 and 0.85 °K.[10] A suppression of $-dT_c/dc = 10$ °K at.% was observed, which is comparable to that found in *Al*Mn and *Al*Cr.[10]

ZnV and ZnCo

We have not been able to find in the literature any measurements on either alloy system, except for *superconductivity* measurements in *Zn*Co, the results of which indicate that Co is nonmagnetic in Zn.

Finally, we take into account the behavior of the *residual resistivity* along the Zn–transition-metal system.[6,7] This shows a broad maximum of about 23 $\mu\Omega$ cm/at.% around *Zn*Mn, thus indicating, according to Friedel's theory, that the virtual bound state of the transitional impurities is never completely magnetic.[34] Previous values of $(\Delta\rho/c)_{4.2\,^\circ\mathrm{K}}$ are 16.5 ± 0.5 $\mu\Omega$ cm/at.% for *Zn*Mn,[7] 12.8 ± 0.5 $\mu\Omega$ cm/at.% for *Zn*Cr,[7] and 15.4 ± 0.3 $\mu\Omega$cm for *Zn*Fe.[7]

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