# Localized Magnetic Impurity States In Metals: Some Experimental Relationships*

M. D. DAYBELL,† W. A. STEYERT
*Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico*

Evidence is reviewed which demonstrates that the recently observed low-temperature electron state arising from the Kondo effect in metals containing small numbers of transition element impurities is present over a much wider temperature range than is generally appreciated. The possibility that this state forms a link between magnetic and nonmagnetic impurity states in metals as suggested by Schrieffer is discussed.

## INTRODUCTION

Recent experimental observations of a new electron state in metals containing a small number of magnetic impurity ions[1–4] have confirmed theoretical predictions[5–20] that a "quasi-bound state" should be formed between the magnetic moment of a localized impurity and the average moment of the itinerant electrons in its vicinity. This state is analogous in some ways to the Cooper pair in superconductors. Evidence based partly on very recent data and partly on a review (in the light of recent theoretical developments) of the earlier literature,[21] shows that the occurrence of the quasi-bound state is much more widespread than is generally realized, and is not strictly a low-temperature phenomenon. Since the temperature $T_K$ below which this state exists depends exponentially on the exchange constant $J$ between the impurity spin and that of the conduction electrons, the possibility that small changes in $J$ can vary $T_K$ from millidegrees to thousands of degrees is not at all unlikely, as has been pointed out recently by Schrieffer.[12]

In the few matrix-impurity systems that have been well-studied experimentally, it is possible to formulate rules which predict the occurrence of quasi-bound states in some alloys for which data are not yet available. Some justification for these rules may be obtained from a slight extension of existing theoretical models. Various fruitful directions for future experimental investigations in solid and liquid metals are discussed.

Section I is a brief noncritical review of some of the theoretical concepts relevant to the experimental observations. Current theoretical activity in this field is quite high, amounting to a few papers a month, and no attempt has been made to cite all the available work although many references to the original literature are given.[22] In Sec. II, the detailed behavior predicted by some of the theories for various experimentally measurable quantities is examined. A description is given of the way in which this information is used to obtain values of certain characteristic temperatures $T_c$ which form *estimates* of $T_K$ for the various alloys for which data are available. The results of this analysis are presented in a series of figures and tables. One way of interpreting the highly systematic variation of $T_K$ with position of the impurity in the periodic table, based on the recent conjectures of Schrieffer,[12] is discussed in Sec. III. The concluding section deals with other questions which the results of the present review may help to resolve, as well as raising a few new ones.

## I. THEORETICAL CONCEPTS

If a dilute alloy **M**–I is formed by dissolving a small number of first-row transition-metal atoms I in a metallic matrix **M**, it is often found that the impurity has a net moment arising from the *d*-shell valence electrons of the impurity. This localized magnetic impurity state has dramatic effects on many of the electronic properties of the alloy. Many of these effects are discussed in a later section, but for the present attention is confined to the properties of the state itself.

Some time ago, Friedel gave a phenomenological

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† Associated Western Universities Faculty Fellow.

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[6] P. W. Anderson, J. Appl. Phys. **37**, 1194S (1966).

[7] K. Yosida and A. Okiji, Progr. Theoret. Phys. (Kyoto) **34**, 505 (1965).

[8] K. Yosida, Phys. Rev. **147**, 223 (1966); Progr. Theoret. Phys. (Kyoto) **36**, 875 (1966).

[9] A. Okiji, Progr. Theoret. Phys. (Kyoto) **36**, 1712 (1966).

[10] J. Kondo, Progr. Theoret. Phys. (Kyoto) **36**, 429 (1966); Phys. Rev. **154**, 644 (1967).

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[14] G. Kemeny, Phys. Rev. **156**, 740 (1967).

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[16] H. Suhl, Phys. Rev. **138**, A515 (1965); Physics **2**, 39 (1965); Phys. Rev. **141**, 483 (1966).

[17] H. Suhl, Phys. Rev. Letters **17**, 1140 (1966).

[18] A. A. Abrikosov, Physics **2**, 5 (1965).

[19] D. R. Hamann, Phys. Rev. **158**, 570 (1967); P. E. Bloomfield and D. R. Hamann, Phys. Rev. **164**, 856 (1967).

[20] H. Ishii and K. Yosida, Progr. Theoret. Phys. (Kyoto) **38**, 61 (1967).

[21] An extensive review by G. J. Van den Berg, in *Progress in Low Temperature Physics*, C. J. Gorter, Ed. (North-Holland Publ. Co., Amsterdam, 1964), Vol. IV, p. 194, discusses the situation before the development of the concept of the quasi-bound state.

[22] The situation up to 1965 is reviewed by M. Bailyn, Advan. Phys. **15**, 179 (1966).

explanation of the local moment in terms of the concept of the "virtual bound state."[23] It was pointed out that the $d$ orbitals of the $3d$-shell valence electrons of a transition-metal atom dissolved in a metal would retain much of their localized character, even when they are embedded in the conduction band of the host material. The effect of the conduction band states on an electron in this localized state could be allowed for, at least to first order, by simply letting the atomic $d$ level be broadened and shifted in energy from its unperturbed value. This shift would be just enough to keep the ionic charge on the impurity equal to that of the host. An electron could not be permanently bound in this virtual state, since it would be able to leak out into conduction band states having similar energies, but most of its wave function would be localized very near to the impurity if the broadening of the virtual level were small.

Another way of treating the interaction of the conduction electrons with the impurity is to reduce the system to an equivalent scattering problem.[23,24] In this picture, the impurity first gives up *all* its $s$ and $d$ valence electrons to the conduction band of the host, creating a strong localized attractive Coulomb potential well which is almost deep enough to have bound $d$ states for every $d$ electron given up. Enhancement of the conduction electron wave functions near the impurity by the resonances that then exist in the $d$-wave part of their scattering cross sections at electron energies near those of the vacated $d$ levels is strong enough to screen out most of the excess positive charge that was left on the impurity when its valence electrons were removed.

To explain the presence of a net magnetization on an impurity, Friedel pointed out that the exchange and correlation effects responsible for Hund's rule (which for a free atom determines the net spin of an atomic $d$ shell containing more than one electron) would operate to separate the energy of the virtual bound state for spin-up electrons from that for those of opposite spin. When the virtual level is narrow enough for this to occur, a net magnetic moment will result in cases where the number of spin-up levels exceeds the number of spin-down levels for energies less than the Fermi energy $E_F$. Using the requirement of electrical neutrality to estimate the occupation numbers of the virtual levels, Blandin and Friedel[23] were able to construct a table predicting whether or not a localized moment would occur in some typical alloys. A recent version[24] is given in Table I.

To put these ideas on a more quantitative basis,

TABLE I. (After Freidel.) Dilute alloy systems for which localized moments are known to occur are represented by +; a − implies that no moment occurs (under the earlier interpretations).

| | Fermi energy increases → | | | | | | |
|---|---|---|---|---|---|---|---|
| | PdH | Au | Ag | Cu | Mg | Zn | Al |
| Sc | | | | | | | |
| Ti | | − | | | | | − |
| V | | + | | | | | − |
| Cr | + | + | + | + | | + | − |
| Mn | + | + | + | + | + | + | − |
| Fe | + | + | | + | + | − | − |
| Co | ? | + | | ? | | | − |
| Ni | − | − | | − | | − | − |

Anderson solved the following simple model in the Hartree–Fock approximation, for temperature $T=0°K$.[25–27] Assume a localized moment exists, and can be represented by a single $d$-orbital level whose energy is a distance $\epsilon_d$ below the Fermi level, so that it is occupied by an electron of say, spin-up. A spin-down electron attempting to occupy the same level will see the full repulsive Coulomb interaction $U$ between it and the $d$ electron already on the impurity, and so could only occupy a level whose energy is $-\epsilon_d+U$, which must be empty by our assumption that a moment exists, and hence lie above the Fermi level. Now, as before, the conduction electrons can, through the $s$–$d$ mixing interaction, $V_{kd}$, mix with the electron in the localized level and cause that level (and the empty level above the Fermi energy) to be broadened and shifted. The broadening of the spin-up level pushes the high-energy tail of its energy distribution above the Fermi level so that it can be partially empty, reducing the average number of localized spin-up electrons to less than one. At the same time, the broadening of the spin-down state allows it to become partially filled. But this decreases the effect of the Coulomb interaction, $U$, and allows the spin-up and spin-down levels to become closer together in energy, so that if the $s$–$d$ interaction is too strong, the configuration becomes unstable, the state collapses to two degenerate levels, and no moment appears. Later work[14,28–32] (taking correlations beyond the HF approximation into account) in fact suggests that only in the case when the spin-up state is nearly always occupied and the spin-down state nearly always empty can a local moment exist. In this situation, unless the virtual level is quite narrow, the two states must be located approximately symmetrically with respect to the Fermi level.

[23] P. De Faget de Casteljau and J. Friedel, J. Phys. Radium **17**, 27 (1956); J. Friedel, Can. J. Phys. **34**, 1190 (1956); J. Friedel, J. Phys. Radium **19**, 573 (1958); A. Blandin and J. Friedel, J. Phys. Radium **20**, 160 (1959).

[24] See, for example, E. Daniel and J. Friedel, in *Proceedings of the 9th International Conference on Low Temperature Physics*, J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub, Eds. (Plenum Press, New York, 1965), p. 933 (Part B).

[25] P. W. Anderson, Phys. Rev. **124**, 41 (1961); P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. **6**, 124 (1961).

[26] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 338.

[27] P. A. Wolff, Phys. Rev. **124**, 1030 (1961).

[28] J. R. Schrieffer and D. C. Mattis, Phys. Rev. **140**, A1412 (1965).

[29] B. Kjöllerström, D. J. Scalapino, and J. R. Schrieffer, Phys. Rev. **148**, 665 (1966).

[30] J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966).

[31] G. Kemeny, Phys. Rev. **150**, 459 (1966).

[32] A. C. Hewson, Phys. Rev. **144**, 420 (1966).

The same $s$–$d$ interaction which shifts the level of the localized spin-up state pulls the energy of the spin-down conduction electron states down into the Fermi sea and pushes the spin-up conduction electron states above it, resulting in a net polarization of the conduction electrons near the impurity. This polarization is antiparallel to that of the $d$ electron on the impurity,[12,25,30,33] resulting in an effective antiferromagnetic exchange interaction (see below). Its value depends on the strength of the $s$–$d$ interaction.

This model has been generalized[12,25,32,34,35] to apply to the more realistic case where there are many degenerate $d$ levels present, although, for simplicity, the orbital angular momentum has usually been assumed to be completely quenched so that the total angular momentum on the impurity becomes just the net spin angular momentum of these localized $d$ electrons. The Hamiltonian for the single $d$-orbital Anderson model can be expressed as

$$H=H_{\text{cond}}+H_{\text{imp}}+H_{\text{kd}}, \tag{1}$$

where $H_{\text{cond}}$ is the unperturbed conduction electron Hamiltonian of the pure matrix metal, $H_{\text{imp}}$ is the full Hamiltonian of the isolated impurity atom (or ion), and $H_{\text{kd}}$ is a one-body operator which allows for the mixing of the conduction electron state $\mathbf{k}$ with an electron in one of the virtual $d$ levels. Normally, $H_{\text{kd}}$ is taken to be of the form

$$\sum_{\text{k}\sigma} V_{\text{kd}}c_{\text{k}\sigma}{}^{+}c_{d\sigma}+V_{\text{kd}}{}^{*}c_{d\sigma}{}^{+}c_{\text{k}\sigma}, \tag{2}$$

where $V$ describes the strength of the mixing, $c_{\text{k}\sigma}{}^{+}$ creates a conduction electron of momentum $\mathbf{k}$, spin index $\sigma$, $c_{d\sigma}$ destroys a $d$ state electron of spin index $\sigma$, and the other quantities are their conjugates. The width of the virtual $d$ levels $\Gamma$ is related to $V_{\text{kd}}$ and $\rho$, the density of states per spin state at the Fermi surface on the host metal, by[24,28]

$$\Gamma=\pi\rho\,|\,V_{\text{kd}}\,|_{\text{av}}{}^{2}, \tag{3}$$

where the average is over $\mathbf{k}$ states at the Fermi surface.

A large part of the recent theoretical activity in the field of localized moments has been based on a sequence of papers by Kondo,[33,36,37] who *starts* with the assumption that a moment exists, and characterizes the impurity by simply assigning it a spin $\mathbf{S}$, which interacts with the conduction electrons through a contact interaction represented by a term in the Hamiltonian

$$H_{\text{ex}}=-J\Omega\mathbf{S}\cdot\mathbf{s}(0) \qquad J<0, \tag{4}$$

where $J$ is the strength of the exchange interaction,[38] $\Omega$ is an atomic volume, and $\mathbf{s}(0)$ is the average conduction electron spin density at the impurity. For a matrix crystal containing $N$ atoms, this may be written in terms of conduction electron creation and annihilation operators $c_{\text{k}\sigma}{}^{+}$ and $c_{\text{k}\sigma}$ as

$$H_{\text{ex}}=-(J/2N)\sum_{\text{k,k}'}[(c_{\text{k}\uparrow}{}^{+}c_{\text{k}'\uparrow}-c_{\text{k}\downarrow}{}^{+}c_{\text{k}'\downarrow})S_z +c_{\text{k}\uparrow}{}^{+}c_{\text{k}'\downarrow}S_{-}+c_{\text{k}\downarrow}{}^{+}c_{\text{k}'\uparrow}S_{+}], \tag{5}$$

where $\mathbf{k}$ and $\mathbf{k}'$ are the initial and final momenta of the interacting electrons, and $S_{\pm}$ are raising and lowering operators for the components of $\mathbf{S}$.

Attempting to evaluate the contribution of this exchange coupling to the electrical resistivity of alloys containing localized moments, Kondo discovered that the exchange scattering cross section diverges at low temperatures, causing the resistivity to increase logarithmically as the temperature approaches absolute zero. When more sophisticated techniques based on many-body perturbation theory,[18] double time Green's functions,[5] or dispersion theory[15,16] were applied to Kondo's Hamiltonian, it was found that below a certain temperature $T_K\simeq T_F\exp(-1/|J|\rho_1)$, now called the Kondo or Suhl–Abrikosov temperature, a new electron state should exist. Here $kT_F=E_F$, and $\rho_1$ is the density of states of one spin index *per atom* in the host metal, evaluated at the Fermi surface. Below this temperature, the high-temperature state consisting of conduction band plus localized moment, modified by the weak perturbational exchange coupling between them, collapses to a "quasi-bound state" whose ground state energy at $T=0°\text{K}$ is approximately $kT_K$ below that of the same system without the coupling.

The transition to the quasi-bound state is broadened in temperature by thermal fluctuations associated with its small number of degrees of freedom. Since $kT_K$ goes to zero more rapidly than any power of $J$ as $J$ approaches zero, these results explained the difficulties with the perturbational approach. Roughly speaking, the quasi-bound state in this picture consists of the bare high-temperature localized spin clothed in a cloud of conduction electron spin polarization tending to cancel its magnetic moment.

Recently, the dispersion theory calculation has been extended into the region surrounding $T_K$,[15] where all of the earlier work had experienced computational difficulties. These authors also emphasize the important role of the influence of ordinary potential scattering from the impurity on the properties of the quasi-bound state, including the value of $T_K$. Silverstein and Duke[39] have demonstrated that below the Kondo temperature, existing theories are valid to at most logarithmic accuracy in the conduction electron energies; to that accuracy, the results of Suhl and Abrikosov are equivalent. These two models, in turn, have been shown to be closely related to that of Nagaoka.[19] (See also a letter

[33] J. Kondo, Progr. Theoret. Phys. (Kyoto) **28,** 846 (1962).
[34] B. Muhlschlegel and J. R. Schrieffer (unpublished work, see Ref. 30).
[35] K. Yosida, A. Okiji, and S. Chikazumi, Progr. Theoret. Phys. (Kyoto) **33,** 559 (1965).
[36] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32,** 37 (1964).
[37] J. Kondo, Progr. Theoret. Phys. (Kyoto) **34,** 204 (1965).
[38] Kondo uses a coupling constant $J_{\text{K}}=J/2$.

[39] S. D. Silverstein and C. B. Duke, Phys. Rev. Letters **18,** 695 (1967).

by Suhl.[40]) It has also been shown that the quasi-bound state can be broken up by applying a magnetic field greater than $H_c$, where $\mu_B H_c \simeq kT_K$, $\mu_B$ = one Bohr magneton.[1,41,42]

Using the exchange model in a simple variational calculation, it can be demonstrated that a spin $\frac{1}{2}$ local moment plus a conduction electron form a singlet in their variational ground state.[8] Such a ground state can also be found in a many-body calculation.[13,20,43] Using a model that results in a spin-degenerate zero-temperature ground state, Kondo has shown that the usual susceptibility obtained at $T=0$ in the singlet calculations,[13,20] $\chi \simeq \mu_B^2/kT_K$, can also be a property of nonsinglet models. Susceptibility results using a Green's function technique show a large reduction in the total moment of the quasi-bound state[5] at low temperatures, as do the experimental data,[1–4] but the question of the existence of a singlet ground state at absolute zero is still open.[19,44]

By performing a canonical transformation on the Anderson Hamiltonian to remove the $H_{kd}$ term to first order in $V_{kd}$, the mixing term can be put into the form of Kondo's exchange Hamiltonian[30] if $\Gamma/\epsilon_d \ll 1$. As mentioned earlier, this is likely to be a good approximation in cases in which localized moments occur at all. The relation between the Anderson model and the exchange model is then expressed by the relation:

$$J/N = -2[|V_{kFd}|_{av}^2 U/(|\epsilon_d| \cdot |\epsilon_d + U|)], \quad <0 \quad (6)$$

where the normalization of $J$ is that of Eqs. (4) and (5).

## II. CHARACTERISTIC TEMPERATURES: THE EXPERIMENTS

Formation of a quasi-bound state of the type discussed by Nagaoka, Suhl, Abrikosov, Yosida, and others[5–20] manifests itself in many of the observable properties of alloys containing localized magnetic impurity states. Theories exist which allow the Kondo temperature $T_K$ appearing as a parameter in various calculations to be related quantitatively to temperatures characteristic of the experimental data but rarely do various theories give the same numerical result. In cases where such relationships exist, they are often directly applicable only for impurity spin values of $\frac{1}{2}$. Moreover, some of the characteristic temperatures ($T_c$) determined from the available experimental data using the formal prescriptions of subsections A, B, C, and D below (see Fig. 1) are uncertain to within factors of two or more, either because of moderately large extrapolations, or because the importance of establishing the lack of impurity–impurity interaction effects was not a consideration in the design of the only relevant

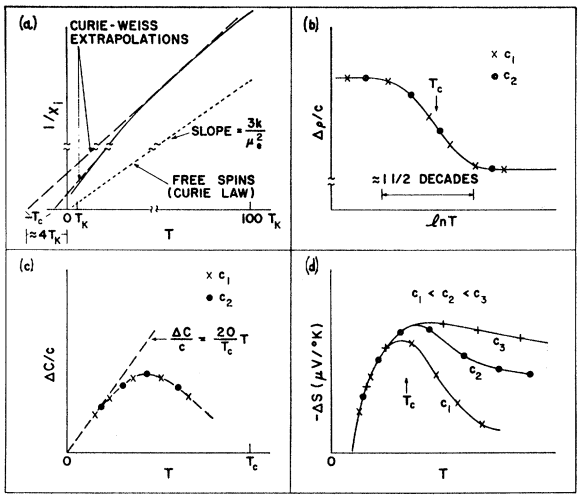


FIG. 1. Typical behavior of the incremental susceptibility, resistivity, specific heat, and thermoelectric power resulting from the addition of various small concentrations $c_1$, $c_2$, and $c_3$ of a magnetic impurity to a nonmagnetic host metal. The features of the inverse susceptibility curve (a) are exaggerated to show small deviations from the Curie–Weiss law, as discussed in the text. It is important to note that $T_c$ is a characteristic temperature used to facilitate the correlation of several properties of the alloys. Its precise relation to the transition temperature $T_K$ appearing in various theories depends on the structure of the theory chosen.

experiments available. As will be seen later, the exponential nature of the variation of $T_c$ from alloy to alloy minimizes the importance of uncertainties of factors of 2, $\pi$, etc. in the theories and in the assigned values of $T_c$. However, the rules used to obtain values of $T_c$ are carefully spelled out, so that the results of the present compilation may be readily compared with theoretical relations other than those used here.

A review of the existing experimental work covering the first-row transition elements as impurities in copper and gold reveals some striking systematic relationships. An understanding of the reasons for these orderly variations of $T_c$ (and hence $T_K$) from alloy to alloy should be useful in explaining the fundamental properties of localized moments in metals. Only for a very few alloys is the complete temperature range of interest in the present problem accessible to experiment, either because $T_c$ is so low that magnetic ordering occurs in any alloy sufficiently concentrated to see the effect of the impurity, or because $T_c$ is so high that melting occurs within the transition region. For this reason, the correlation of measurements of many different properties of many different alloys provides strong experimental support for some current models that was not available from data on individual systems. This strong correlation between the $T_c$'s determined from widely different properties of a single alloy lends credibility to the theories upon which the interpretation is based.

In obtaining characteristic temperatures from experimental data, preference was given to information obtained from the most dilute alloys studied, so long as

[40] H. Suhl, Phys. Rev. Letters **18**, 743 (1967).
[41] B. Giovannini, R. Paulson, and J. R. Schrieffer, Phys. Letters **23**, 517 (1966).
[42] P. Gaidukov, Zh. Eksperim. i Teor. Fiz. **34**, 836 (1958) [English transl.: Soviet Phys.—JETP **34**, 577 (1958)].
[43] J. Kondo (preprint).
[44] P. W. Anderson, Phys. Rev. **164**, 352 (1967).

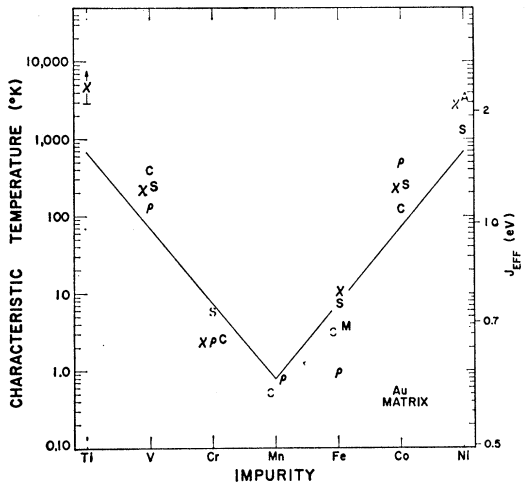


FIG. 2. Characteristic temperatures for first-row transition elements in gold. Values are obtained from data in alloys sufficiently dilute that impurity–impurity interactions are not important, and therefore are properties of the impurity-matrix interaction itself. Symbols used to represent each type of measurement are: susceptibility, $\chi$; resistivity, $\rho$; specific heat, **C**; thermoelectric power, **S**; Mössbauer, **M**; and infrared absorption, **A**. Light broken symbols indicate a result uncertain to more than a factor of 2. The temperatures $\chi$ and **M** are probably high estimates of $T_K$ (see text). $J_{\text{eff}}$ is from Eq. (10), using $\rho_1=0.15$ eV$^{-1}$ atom$^{-1}$ in both gold and copper. Straight lines represent Eq. (14).

enough of the impurity was present to permit a meaningful number to be obtained. Every attempt was made to establish concentration independence of the contribution per impurity of each property of each alloy (see appendix). In this way impurity–impurity interaction effects appearing at low temperatures were largely avoided.

### A. Susceptibility

Perturbation calculations of the temperature-dependent part of the susceptibility contribution of each impurity approach the limit $\chi_i=\mu_e^2/3kT$ at temperatures far above $T_K$.[45,46] Here $\mu_e$ is the effective number of Bohr magnetons, $\mu_e^2=g^2[S(S+1)]\mu_B^2$, of an impurity of spin $S$, Landé $g$ factor $g$. Below $T_K$, no detailed calculations of $\chi_i$ have been made except for its value at $T=0$,[5,19,20,43] which, according to several authors[20,43] can be taken as approximately $\mu_e^2/3kT_K$. A Curie–Weiss law of the form

$$\chi_i=(\mu_e^2/3k)\,(T+T_K)^{-1} \qquad (7)$$

is a convenient choice for an interpolation formula between these two limits, and Kondo[43] has recently given theoretical reasons for expecting the susceptibility to be of this form. Values used in the present analysis for the temperatures characteristic of the susceptibility were obtained by fitting a law of the above form (with $T_c$ substituted for $T_K$) to the data, and are represented in Figs. 2–4 by the symbol $\chi$.[47] Usually, $T_c$ was obtained by plotting the reciprocal of the susceptibility per impurity atom versus $T$, and extrapolating to $1/\chi_i=0$,[48] where $T=-T_c$ [Fig. 1(a)].

### B. Resistivity

Theory[5,15,19] and experiment have shown that the thermal breakup of the quasi-bound state with increasing temperature will generally be accompanied by a drop in the impurity contribution to resistance ($\Delta\rho=\rho_{\text{alloy}}-\rho_{\text{pure}}$) as shown in Fig. 1(b). (The resistance of the host, $\rho_{\text{pure}}$, increases with $T$, primarily because of electron–lattice scattering.) Ideally, the characteristic temperature could be taken at the mid-

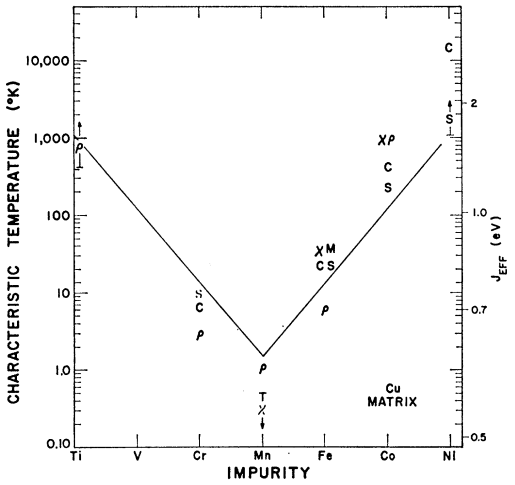


FIG. 3. Characteristic temperatures for first-row transition elements in copper. See Fig. 2 caption.

[45] D. J. Scalapino, Phys. Rev. Letters **16**, 937 (1966).

[46] D. R. Hamann, Phys. Rev. Letters **17**, 145 (1966); L. Dworin, *ibid.* **16**, 1042 (1966).

[47] $\chi_i=(\chi_{\text{alloy}}-\chi_{\text{pure}})$ per gram divided by the number of impurity atoms per gram. In these matrices $\chi_{\text{pure}}$ is an approximately temperature independent negative quantity.

[48] It should be pointed out that one can do better than this in individual cases by using the complete expression for $\chi$ from perturbation theory (Ref. 45) which can be put in the form:

$$1/\chi_i=[\mu_e^2/3kT_K]^{-1}\tau[\ln\tau/(\ln\tau-1)],\ [\tau=T/T_K].$$

This expression, shown schematically in Fig. 1(a), is a very slowly varying function of $\tau$ above $\tau=8$, being slightly concave downward above $\tau=15$. It has a divergence at $\tau=e$, and is probably unphysical below about $\tau=10$. The true $1/\chi_i$ function is expected to drop at $T=0$ to at least $[\mu_e^2/3kT_K]^{-1}$ and possibly to 0. Making the reasonable assumption that the curve remains concave downward *throughout* its range, and using the known behavior of the CuFe susceptibility (Refs. 4 and 49) as a model in the region near $T_K$(or $\tau=1$), it is possible to draw the solid curve shown. For the range of temperatures covered in a typical experiment carried out above about $3T_K$, this function approximates a Curie–Weiss law quite well. In general, this law will have the form:

$$\chi_i=[(a\mu_e)^2/3k]/(T+bT_K),$$

where for the range $4T_K<T<100T_K$, for example, $a=0.90$, $b=4$. Thus, for low values of $T_K$, $T_c$ determined from the Curie–Weiss law probably overestimates $T_K$ by a factor of four, while the values obtained for $\mu_e$ underestimate the true effective moment by about 10%. These model-dependent corrections have not been applied to any of the numbers presented in this paper but should be kept in mind.

[49] C. M. Hurd, J. Phys. Chem. Solids **28**, 1345 (1967); Phys. Rev. Letters **18**, 1127 (1967).

point of the ramp. However, except for **Cu**–Fe [4], **Cu**–Cr [49a] and possibly **Zn**–Mn [50] only the high- or low-temperature knee of the expected curve is seen. By assigning a height to this step we can estimate the midpoint when only a portion of the curve is known.

In the absence of a comprehensive theory the height of the step has been taken to be independent of the impurity material.

The change at the step is observed to be 0.14 nΩ-cm/at ppm (1.4 $\mu$ Ω-cm/at.%) in Cu, and calculated to be 0.16 nΩ-cm/at ppm in Au and 0.07 nΩ-cm/at ppm in Mg, Cd, and Zn, using the prediction[5,19] that the step height scales as $E_F^{-1/2}$. The characteristic temperature ($\varrho$ in Figs. 2–4) is *defined* as the temperature at the point where $\Delta\rho$ has increased or decreased from its temperature independent value by $\frac{1}{2}$ the size of the above change.

### C. Specific Heat

A peak is anticipated in the excess specific heat ($\Delta C$) between $T=0$ and $T=T_K$ associated with the thermal destruction of the quasi-bound state [Fig. 1(c)].[5,19] This peak is clearly observed at 6°K in **Cu**–Fe.[51,52] Moreover, the entropy associated with the state,

$$S=\int_0^{T_K} \Delta C/T dT,$$

is found to be $R\ln 2$ per mole of impurity. A similar peak is suggested in **Cu**–Cr [52,53] specific heat data, where $S$ is $R\ln 2.5$ per mole of impurity. ($R$ is the gas constant per mole.)

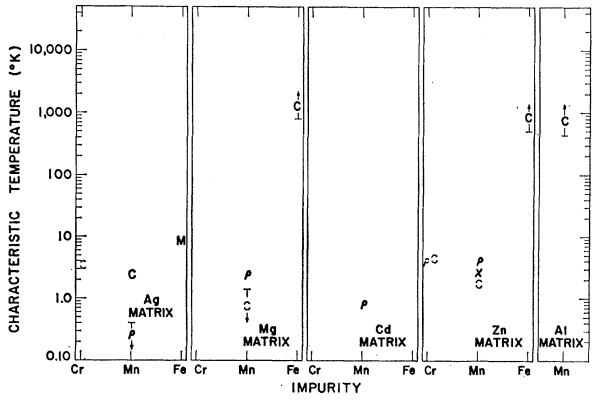


FIG. 4. Characteristic temperatures for first-row transition elements in silver, magnesium, cadmium, zinc, and aluminum. See Fig. 2 caption.

Nagaoka predicts that

$$\Delta C/cT \mid_{T\to 0} \to 2.39R/T_K, \qquad (8)$$

where $c$ is the impurity concentration. A similar expression has been obtained by Kondo,[43] with a constant of 6.6 instead of 2.39. Thus, by observing $\Delta C/cT$ at sufficiently low $c$ to avoid impurity–impurity interaction effects and for $T \ll T_K$, we can arrive at another characteristic temperature (**C** in Figs. 2–4) by using $T_c$ for $T_K$ in Eq. (8). Other theories[19,44] predict a different $T$ dependence of $\Delta C/c$ as $T\to 0$, and it has been pointed out[53a] that an approximation made by Nagaoka casts some doubt on his calculation of this quantity. Because the energy of a system is such a fundamental quantity, specific heat measurements should reveal much about the bound state, making these $T_c$'s of basic importance. Unfortunately, arriving at numbers for **C** based on its definition involves more interpretation and uncertainty than any of the other characteristic temperatures. This is because the measurements must be made at low temperatures (generally less than 20°K) and high concentration (generally greater than 0.1%) so that $\Delta C$ is not completely masked by the host specific heat. Hence, it is hard to be completely free of impurity–impurity interactions for spins with large magnetic moments at low temperatures (i.e., systems with $T_c<100$°K).

For systems with higher $T_c$'s, however, interactions are not so important and the $\Delta C \propto cT$ behavior of the low-temperature limit is seen. This appears as an increase in the electronic specific heat parameter $\gamma$ ($C=\gamma T+aT^3$). In the past this change has generally been interpreted from the band theory point of view as due to a change, $\Delta\rho_1$, in the density of electronic states ($\rho_1$) at the Fermi surface. It has been observed, however, that the $\Delta\rho_1$ obtained from what has been considered to be a change in the Pauli susceptibility upon alloying differs by a factor of about 4 from the $\Delta\rho_1$ arrived at from the change in $\gamma$, both in **Cu**–Ni [54] and **Au**–V.[55] Considering the observed changes in $\chi$ and $\gamma$ as due to the high temperature bound state phenomenon is one way of resolving this discrepancy.[56]

### D. Thermoelectric Power

Suhl and Wong[15] predict that there will be a concentration independent peak in the thermoelectric power of a dilute magnetic alloy near $T_K$. In practice, enough of the magnetic impurity must be present for its exchange scattering contribution to dominate the thermopower, in which case a dramatic peak is observed whose

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[54] E. W. Pugh, B. R. Coles, A. Arrott, and J. E. Goldman, Phys. Rev. **105**, 814 (1957).
[55] F. J. du Chatenier, J. de Nobel, and B. M. Boerstoel, Physica **32**, 561 (1966).
[56] Equation (7) is used for $\Delta\chi_i$ with the $T_c$ (=16 000°K in **Cu**–Ni and 400°K in **Au**–V determined from the $\Delta C$ data. The magnitude of $\Delta\chi_i$ can be fit by a value of 3.2 $\mu_B$ for $\mu_e$ in both systems. See also a complementary scheme by A. P. Klein and A. J. Heeger, Phys. Rev. **144**, 458 (1966).

magnitude and position are more or less independent of concentration and whose shape is approximately gaussian in log $T$, as predicted. At high concentrations the shape of the peak changes, as shown schematically in Fig. 1(d), so that some judgment enters into choosing the proper range of concentrations from which to obtain a characteristic temperature, at least if high accuracy is desired.[57] The temperature at which the peak (denoted by **S** in Figs. 2 and 3) occurs in a suitably chosen concentration range of the alloy is defined as the $T_c$ for the thermopower. The effect of the small and positive increase of the thermopower of the host metal with $T$ is unimportant and has been ignored.

### E. Other Measurements

Using the Mössbauer effect, the magnetic character of dilute Fe impurities in various host matrices can be studied. The effective internal magnetic field, $H_i$, at the Fe nucleus due to polarization of its electronic environment is measured in an external magnetic field. This polarization deviates appreciably from its high temperature $1/T$ behavior at a characteristic temperature (**M** in Figs. 2–4) given by the phenomenological parameter $[(J+1)/J]s$ used in the Mössbauer work.[58] However, $H_i$ does not differ significantly from its high temperature $1/T$ behavior until $T$ is down to about a third of this characteristic temperature so that **M** is probably a high estimate of $T_K$.

A peak appears in the infrared absorption by **Au**–Ni films[59] at photon energies which vary from 0.5 to 0.8 eV as $c$ is varied from 3.9% to 10.2%. Its magnitude is proportional to $c$. Our linear extrapolation of that data indicates that the position of the peak as $c \to 0$ would be 0.32 eV corresponding to a 3700°K binding energy for the quasi-bound state in **Au**–Ni (**A** in Fig. 2).

The tunneling of electrons from a superconductor to a dilute alloy can be used to observe the expected anomaly in the density of states at the Fermi surface in these alloys.[60,61] The quasi-bound states also affect other properties of dilute alloys such as thermal conductivity, expansion coefficient, ESR, NMR, DeHaas–Van Alphen and Hall effects, superconducting transition temperatures, and magnetoresistivity.[21]

## III. A SIMPLE MODEL

Almost none of the theoretical effort dealing with the localized moment problem has been concerned with the problem of predicting the magnitude of the Kondo coupling constant $J$, or its behavior as a function of the position of a given impurity in the periodic table (see, however, Ref. 62). As Suhl[15,16] has pointed out, even knowing $J$ would not imply that $T_K$ could be calculated directly from the expression

$$T_K \simeq T_F \exp(-1/|J|\rho_1) \tag{9}$$

since effects caused by potential scattering off of the same impurity responsible for the exchange scattering will modify the above formula. Nevertheless, it is useful to use the above expression to *define* an effective exchange constant $J_{\text{eff}}$ by

$$T_K = T_F \exp(-1/|J_{\text{eff}}|\rho_1). \tag{10}$$

For an estimate of $J_{\text{eff}}$, we ignore the possibility that it may differ significantly from $J$, and turn to a recent calculation by Schrieffer[12] in which, by applying the canonical transformation technique[30] to a generalization of the Anderson model that accommodates all ten $d$ electron levels, an expression is obtained which can be used to find the dependence of $J$ on the total spin value of the "bare" localized moment. In that paper, it is pointed out that $J$ should arise primarily from a resonant interaction between the $d$-wave part of the conduction electron wave functions and the localized $d$ states on the impurity, rather than from the $s$-wave–$d$-state interaction assumed in most other calculations.[63] The $n$ $3d$ electrons of the impurity are assumed to occupy the available $d$ level according to Hund's rule, so that the localized spin $S=n/2$ for $n \leq 5$, and is $(10-n)/2$ for $n \geq 5$. The $n_u$ $(=2S)$ unpaired electrons go into the $d$ orbitals of angular momentum magnetic quantum number $m_1=L$, $m_2=L-1$, $m_3=L-2\cdots m_{n_u}$; the ground state of the unperturbed impurity is an eigenstate of the total orbital angular momentum operator, $L^2$. Spin–orbit and orbital exchange interactions with the conduction band are neglected. Schrieffer points out that with these assumptions, only conduction electrons having the same $d$-wave magnetic quantum number, $m$, as one of the singly occupied $d$ orbitals on the impurity can undergo spin–spin exchange scattering of the Kondo type. Under these conditions,

$$J_m/N = -[|V|^2/|\epsilon_m|][U/|\epsilon_m + U|][2S]^{-1}, \tag{11}$$

where $U$ and $V$ are analogs of the Coulomb and $s$–$d$ mixing integrals of the single orbital Anderson model, although here $V$ is expressed in terms of conduction band states which are eigenfunctions of the orbital

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[57] Ideally a sequence of Nordheim–Gorter diagrams [see D. K. C. MacDonald, *Thermoelectricity* (John Wiley & Sons, Inc., New York, 1962), p. 109] for various concentrations of impurity at several temperatures would be used to extrapolate the thermoelectric power at each temperature; the peak in the graph of the values obtained vs. the temperature would then be taken as $T_c$.

[58] T. A. Kitchens, W. A. Steyert, and R. D. Taylor, Phys. Rev. **138**, A467 (1965).

[59] F. Abeles, in *Metallic Solid Solutions*, J. Friedel and A. Guinier, Eds. (W. A. Benjamin, Inc., New York, 1963), Chap. 17, p. 1.

[60] F. T. Hedgcock and C. Rizzuto, Phys. Letters **24A**, 17 (1967).

[61] J. A. Appelbaum, Phys. Rev. Letters **17**, 91 (1966); Phys. Rev. **154**, 633 (1967); P. W. Anderson, Phys. Rev. Letters **17**, 95 (1966).

[62] R. E. Watson, S. Koide, M. Peter, and A. J. Freeman, Phys. Rev. **139**, A167 (1965).

[63] See Refs. 12 and 62 for a further discussion of this point.

angular momentum, rather than Bloch functions. The constant $J_m$ is the analog of $J$ in Eq. (5) and can be defined by replacing the conduction electron operators in that equation by those for band states of angular momentum $l=2$, $l_z=m$, wave number $k$, spin $\pm\frac{1}{2}$. The Kondo temperature is still given by Eq. (9), with $J$ replaced by $J_m$. The energy required to remove an electron from a singly occupied $d$ orbital and place it at the Fermi energy, $-|\epsilon_m|$, is assumed to be independent of $m$. Using the fact that $\epsilon_m \simeq -U/2$ if a localized moment is to occur at all in the Anderson model (unless the virtual level is quite narrow),

$$J_m\rho/N=-2\rho\,|\,V\,|^2/n_u\,|\,\epsilon_m\,| \qquad (12)$$

or, by comparison with Eqs. (3) and (6),

$$|\,J_m\,|\,\rho_1=4\Gamma/n_u\pi\,|\,\epsilon_m\,|. \qquad (13)$$

Using these results of Schrieffer's analysis, we make the simplest choice of $\Gamma/|\,\epsilon_m\,|$ consistent with the features of the experimental results, and set it equal to a constant, independent of the position of the impurity atom in the first row transition series. Inserting Eq. (13) in Eq. (7) gives:

$$\ln T_K=-\pi(|\,\epsilon_m\,|/4\Gamma)n_u+\ln T_F. \qquad (14)$$

If $n_u$ is alloyed to change in integer steps starting at 2 in titanium, increasing to 5 in manganese, and then decreasing to 2 again in nickel, the curves shown in Figs. 2 and 3 are obtained when $\Gamma/|\,\epsilon_m\,|$ is taken to be 0.306 in copper and 0.309 in gold.

Several features of this admittedly crude calculation should be pointed out. First, it provides a very good qualitative description of the impurity dependence of $T_K$. In the two systems examined, $\Gamma/|\,\epsilon_m\,|$ is nearly constant; allowing it to vary by $\pm 15\%$ from impurity to impurity would bring the predictions of the model into quantitative agreement with the experiments. The half-width $\Gamma$ of the virtual level is only about 30% of its distance below the Fermi level, so that the requirements for the exchange model to be equivalent to the Anderson model are reasonably well satisfied. Since $\ln T_F$ varies only slightly on the scale of Figs. 2–4 as the Fermi energy changes from 5.5 (for gold) to 14 eV (for aluminum), the principal effect of Friedel's assumption[23,24] that $\Gamma/|\,\epsilon_m\,|$ increases with $E_F$ is to push the center of the V-shaped curve upward at higher Fermi energies while its ends remain fixed. This is consistent with Schrieffer's explanation of the behavior of the room-temperature residual resistivity of dilute alloys of the first-row transition elements in aluminum, in which it is assumed that the Kondo temperature of each of these alloys lies above the temperature of the measurements.[12] On this model, the aluminum alloys form a degenerate case of the class of materials discussed above. In the aluminum system, moreover, the maximum value of $n_u$ occurs near chromium rather than near manganese, where it apparently occurs in copper and gold alloys. This may be explained by valency effects arising from the smaller electronegativity of aluminum, which would tend to increase the number of $d$ electrons on the transition impurities.

Such a trend in the position of the maximum value of $n_u$ with electronegativity also seems to be present in the fragmentary data on the other systems shown in Fig. 4, and possibly even in copper, where it appears that the "vee" curve in Fig. 2 might better represent the results if $n_u$ were allowed to reach its maximum somewhere *between* chromium and manganese.

## IV. DISCUSSION

By examining the experimental literature covering a few relatively well-studied alloy systems in the light of recent theoretical ideas, it has been possible to assemble a great deal of evidence for the conjecture that the Kondo effect, and in particular the quasi-bound state, forms the link between magnetic and nonmagnetic impurities in metals. The beginnings of a quantitative understanding of the mechanism involved, contained in a crude model involving many simplifying assumptions, make it possible to predict, in systems for which sufficient information exists, the temperature $T_K$ near which the transition between these two types of states will occur. Experiment and theory together make it clear that the quasi-bound state phenomenon is widespread, and is definitely not restricted to low temperatures.

These developments make it necessary to revise the picture of transition metals as impurities in metals. A few alloys, like **Cu**–Co and **Au**–Co, which have been considered to be nonmagnetic,[64] must be considered from this more general point of view. Information presented here should be useful in reaching a better theoretical understanding of the dependence of properties of dilute alloys such as residual resistivity on the position of the impurity in the periodic table. Experiments[65] in ternary alloys where local moments on a transition-metal impurity appear and disappear as the electron concentration of the binary matrix is varied may be explained by the rapid variation of $T_K$ with $J_{\text{eff}}$.

The Kondo effect is apparently not sensitive to the state of order of the matrix, as evidenced by its existence at temperatures where lattice vibrations dominate the electrical resistance and specific heat, and by the fact that resistivity minima have been seen in copper–gold alloys containing traces of iron, and these minima remain even when the alloy is transferred from the ordered to the disordered phase.[66] It would be surprising

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TABLE II. Measured effective magnetic moments $\mu_e$ of transition metal impurities in various matrices, expressed in Bohr magnetons. $\mu_e = g[j(j+1)]^{1/2}$, where $j$ is the total impurity angular momentum and $g$ is the Lande $g$ factor.

| Matrix | V | Cr | Mn | Fe | Co |
|---|---|---|---|---|---|
| Au | 3.1[a] | 4.0[b] | 5.8[b] | 3.7[e] | 4.5[d] |
| Ag | | | 5.6[e] | | |
| Cu | | 3.9[f] | 4.9[g] | 3.7[e] | 3–5[d] |
| Cd | | | 3.8[h] | | |
| Zn | | | 3.9[i] | | |
| Mg | | | 5.2[j] | | |

[a] Reference 3.
[b] Reference 69.
[c] Reference 49.
[d] Reference 70.
[e] Reference 71.
[f] Reference 72.
[g] Reference 21.
[h] Reference 50.
[i] Reference 74.
[j] Reference 75.

if dilute alloys of liquid metals did not exhibit a Kondo effect as well.

There are some oversimplifications in the picture presented in Sec. III. In **Au**–Fe, for example, the residual resistivity begins to drop again a few hundred degrees below its melting point,[67] while in at least one typical nontransition metal alloy, **Au**–Al, it is rising in this region.[68] Other data (particularly the susceptibility) are not consistent with this being some sort of "second Kondo effect," and it may even be an oxidation or metallurgical problem. More data are needed.

Another problem is that the simple choice made for $n_u$, the number of unpaired spins, in Sec. III is only in qualitative agreement with the spin values determined from susceptibility results[3,21,49,50,69–75] (Table II).

Some of these discrepancies undoubtedly arise from the fact that a large percentage of the measurements available are not ideally adapted to the type of analysis needed to discuss the Kondo effect. Much experimental work needs to be done on each of the alloys in which a localized magnetic state is believed to exist, with appropriate care taken to establish absence of problems caused by interactions, precipitation of solute on cooling, oxidation of the impurity caused by overlong annealing[76–78] (even in a good vacuum), and other spurious effects. Studies using a binary alloy as the matrix would be of interest, as would data on liquid metals. Other transition metals and the rare earth series as solutes have not yet been extensively studied. The combination of the Kondo effect with superconductivity, using suitable solvent metals, is beginning to be investigated, but certainly much more of interest remains to be learned.[79,80]

Another interesting question involves alloys such as Fe in **Rh** and **Ir** where the impurity contribution to resistance increases with increasing temperature.[81] This has been discussed in terms of a positive $J$. However, these alloys show a susceptibility like that of Fig. 1(a), indicating a very substantial *decrease* in the magnetic moment at low temperatures.[82] Low concentrations of Fe in **Rh** show a specific heat anomaly at low temperatures,[81] and there are Mössbauer anomalies similar to that in **Cu**–Fe in the **Rh** and **Ir** systems.[58,83] Thus, except for resistivity, these results look like the negative $J$ systems. Apparently, quasi-bound state formation in these transition metal hosts decreases the scattering of their $d$-band conduction electrons, but these systems are only beginning to be understood.[83a]

The analysis of the experiments has reached the point where more detailed theoretical expressions for the various measurable quantities for all temperatures are needed, with careful attention to numerical details and, where possible, estimates of the magnitude of important theoretical parameters. More theoretical results are needed for impurity spin greater than $\frac{1}{2}$.

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## APPENDIX

*Susceptibility data.* Concentration-independent values for $T_c$ could be accurately determined for **Au**–Fe,[49,69,71] **Au**–Co,[70] **Au**–Cr,[69] **Cu**–Fe,[49] **Cu**–Co,[70] and **Zn**–Mn,[74] where a number of low concentration alloys gave the same $T_c$. The impurity susceptibility of **Au**–Ti [84] and **Au**–Ni [85] above 100°K showed little temperature variation, thus the extrapolation [Fig. 1(a)] to $1/\Delta\chi_i=0$ is inaccurate, as indicated in Fig. 2. In **Au**–V [3] only a 1% alloy has been studied, but interactions should not be important at this concentration in the temperature range of interest, i.e., 200° to 900°K. For **Cu**–Mn,[21] alloys of 0.029% Mn show $T_c=0\pm0.5$°K, while a factor of 6 or 7 increase in $c$ changes this value only slightly. Thus $T_c$ at the zero concentration limit is unlikely to be greater than 0.5°K, as indicated in Fig. 3.

*Resistivity data.* Clear concentration-independent values for $T_c$ are readily obtained for **Au**–Fe,[86–88] **Au**–Co,[67] **Au**–Mn,[86] **Au**–V,[3] **Au**–Cr,[86] **Cu**–Fe,[67,89,90] **Cu**–Mn,[89] **Cu**–Co,[67] **Cu**–Cr,[49a] **Mg**–Mn,[91,92] **Cd**–Mn,[50] and **Zn**–Mn.[50]

In **Ag**–Mn[93] a long extrapolation of the $\Delta\rho$ vs ln $T$ curve is required, hence only an upper limit on $T_c$ can be estimated. For **Zn**–Cr,[94] $T_c$ is estimated by comparing its behavior to results obtained in **Zn**–Mn in the same experiment.

*Specific heat.* No difficulty is encountered in establishing limiting low $T$ and $c$ values of $\Delta C/T$ in **Au**–Co,[95] **Au**–V,[55] **Cu**–Fe,[51,52] **Cu**–Co,[52,96] and **Cu**–Ni.[52] In some cases, however, it was not clear how to extend to $T=0$ the lowest temperature data for which interaction effects are absent. To assist in this extrapolation to $T=0$, $\Delta C/T$ curves of the alloy under consideration were assumed to be similar to the well established **Cu**–Fe curves. The area under the extrapolated curves was measured to be sure that $\int\Delta C/cTdT=S$ lay in the range from $R\ln 2$ to $R\ln 5$ ($0.7R$ to $1.6R$). For **Cu**–Cr,[52,53] and **Ag**–Mn,[52,97] this extrapolation is small, but in **Au**–Cr[55] the extrapolation is much more difficult; nevertheless, the $T_c$ arrived at is probably correct to within a factor of 2.

The extrapolation in the cases of **Au**–Fe,[55,98] **Au**–Mn,[53,55] **Ag**–Cr,[52] **Mg**–Mn,[99] **Zn**–Cr,[52] and **Zn**–Mn [52] is uncertain to more than a factor of 2 as indicated in Figs. 2, 3, and 4. The lower limit of $T_c$ for **Zn**–Fe [52] is based on a measured $\gamma$ of 0.65 mJ/mole°K$^2$ for a 0.1% alloy compared to values primarily between 0.60 and 0.65 for the most recent measurements on pure Zn.[100] A 0.045% alloy of Mn in **Al** has a $\Delta C/T$ value of less than $5\times10^{-6}$ cal/mole°K$^2$,[101] implying $T_c>450$°K.

*Thermoelectric effect.* A thermoelectric power peak is clearly seen in **Au**–Co,[102] **Au**–Fe,[86,103,104] **Au**–V,[68] **Cu**–Co,[105] and **Cu**–Fe.[105,106] In **Au**–Ni [107] measurements have not been made at enough concentrations to establish $T_c$ to much better than a factor of 2. In the case of **Au**–Cr [86] the alloys measured may be concentrated enough that ordering effects are occurring. For **Cu**–Cr we have averaged the different values from Refs. 89 and 105. The thermopower for the **Cu**–Ni [105] system is still decreasing rapidly at 1000°K toward an apparent negative peak above its melting point.

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