$J'_{ij}\vec{S}_i\cdot\vec{S}_j$, where J'_{ij} depends on the parameters of the conduction electrons and on the distance between the ions i and j.[11] However, because of the nonlinear response of the conduction electrons to the effective field of the localized spins in our theory, the Hamiltonian (2), if expressed in terms of an exchange interaction between the spin operators of the magnetic ions, would contain terms of higher orders in the product $\vec{S}_i\cdot\vec{S}_j$ than the bilinear term in the RKKY Hamiltonian. It is well known[20,21] that such terms can produce first-order magnetic phase transitions.

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Magnetic Properties of 3*d* Transition-Metal Impurities in Metallic Host Lattices[*]

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We report magnetic susceptibility studies of dilute liquid alloys containing V, Cr, Mn, Fe, Co, and Ni in Cu, CuZn, Zn, ZnGa, Ga, GaGe, Ge, GeAs, and As liquid solvents. An analysis of the susceptibilities in terms of excited local impurity configurations (excited impurity pseudoatoms) offers a quantitatively successful and conceptually clear insight into the magnetic properties of impurities in simple metallic host lattices at high temperature.

I. INTRODUCTION

Much still remains to be learned about magnetic ions dissolved in metals. Until recently, the high-temperature static properties of 3*d* magnetic ions such as Fe, Mn, Cr, etc., dispersed in good metallic host lattices were thought to be reasonably well understood in terms of Hartree-Fock models similar to those employed in the description of nonmagnetic ions. Hartree-Fock models of the type proposed by Friedel[1] and later elaborated with a different content by Anderson[2] show that local-moment formation depends on the balance between the local electron-electron interaction energy and the kinetic energy of promotion in a manner very similar to that displayed in Stoner's[3] theory of band ferromagnetism. In this approximation the ionic field distorts the host one-electron wave functions into a self-consistent form that resembles free-impurity-ion wave functions in the neighborhood of the impurity in the metal. It is as if the ionic *d* levels resonate with band states, and the mixing, for the main part, merely modulates band states of appropriate symmetry and in a narrow range of energies, so that they possess an enhanced *d*-like character at the impurity.[1] However, some deepening of these ideas to include host-spin–local-spin coupling has been enforced by the observation of relatively small, but experimentally significant, increases of residual resistance with decreasing temperature at low ambient temperature. This connection was first discussed by Kondo.[4]

Subsequent theoretical and experimental studies have been abundant, but have not yet uncovered a complete and conceptually clear description of the structure of magnetic ions. Both aspects of the investigation have encountered difficulties.[5] The theory is so complex that most studies employ oversimplified descriptions. In one theoretical route it is assumed that the conduction-electron spin $\vec{s}$ couples to the impurity spin $\vec{S}$ antiferromagnetically, with an interaction $\mathcal{H}=J\vec{s}\cdot\vec{S}$, and it has been found that below some "Kondo temperature" T_K the local spin is partly compensated by a local redistribution of the host band spin. Thus, an ion that is magnetic in the Hartree-Fock sense has its moment reduced at low temperatures by interaction with the conduction band. An alternative theory[6] assumes that the impurity ion is nonmagnetic in the Hartree-Fock sense at low temperatures, but, being close to instability, suffers large fluctuations in spin density. According to this approach, the spin fluctuations become indistinguishable from local moments when, at elevated temperatures, the spin fluctuation lifetime exceeds the lifetime against thermally induced reorientation of the incipient local spin.

Experimental studies of magnetic impurities at low temperatures, directed at a number of physical properties other than resistivity, have often yielded conflicting and inconclusive results. In many cases these difficulties have been traced to the major effect of interactions between impurities, through the electron gas, coupling neighboring spins. Thus, the susceptibility of the "classic" Kondo system Fe in Cu is found to contain very large components depending on c^2, with c the impurity concentration.[7] While there remains the likelihood that many other anomalous properties may indeed accompany the well-established resistivity minimum associated with spin-flip scattering (the Kondo effect), one further point appears established beyond doubt. Stassis and Shull[8] have recently shown from careful neutron-scattering investigations that the Fe local moment exists in Cu with a form factor essentially unmodified from the atomic distribution down to temperatures of 4 °K. Further, the magnetization from these atomiclike local moments accounts for the entire observed bulk susceptibility. Thus, any contribution to the bulk susceptibility from "spin compensation" is undetectable at 4 °K. This important result also leads to some difficulty in the alternative approach from linear-spin-fluctuation theory. If the local-moment distribution is so dense and so atomic in form, then the local system can hardly exhibit the structureless linear fluctuations demanded by the theory. On the contrary, it is to be anticipated that electron interactions inside the defect cell must cause quasi-ionic configurations, similar to those of free ions, to be favored.[9] Our more detailed later discussion dwells further on this point. For the moment, however, we return to discuss further coarse features of the local-moment problem.

It is not our principal purpose in this paper to illuminate the subtle questions raised by the anomalous low-temperature properties of magnetic ions. Rather, our aim is to introduce a note of caution into the interpretation of high-temperature phenomena. As mentioned above, there exists a substantial belief that 3*d* impurities, when nonmagnetic (e.g., Mn in Al[1]), may simply be Kondo systems at temperatures below the Kondo temperature T_K at which spin compensation occurs.[5] Before succumbing to this belief, it is best to acknowledge that several alternative causes having overtly chemical origins may independently cause the spin magnetism to be quenched. It is to examples of this behavior that we now turn.

In considering the transition from the magnetic to the nonmagnetic state, whether induced by modifications of host properties or by temperature change, we must first recognize the possible existence of a variety of alternative persistent configurations for any impurity. In Hartree-Fock theory all but one appear as excited configurations of the entire metal, lifetime broadened by recombination. Very little is known at present about excited impurity states in metals, but in certain cases we can point to the existence of well-defined and relatively sharp excited local configurations. These can be classified as (i) excitations inside unfilled cores, (ii) core-to-valence transfers, (iii) localized valence excitations, and (iv) possible local plasmons. The first three lead to configurations that may aptly be described as *excited pseudoatoms*. The two examples that follow will provide an illustration of our later treatment of 3*d* impurities.

a. Core holes. An extreme example is provided by the case of excitations that take an electron from a deep core level to the conduction band in pure metals and alloys. There exist sharp absorption and recombination edges, such as the L_{23} edges of Na, Mg, Al, Si,[10] and MgAl alloys,[11] that point clearly to the existence of well-defined relaxed excited states having a 2*p* core level vacant and the local charge excess screened by the electron gas. We mention that the excitation energy can be calculated with considerable accuracy (to 1%) by a self-consistent application of standard Hartree-Fock methods (corrected for correlation) to the core electrons and linear-response theory combined with pseudopotential methods for the conduction band.[12] This excitation falls in type (ii) above.

b. Rare earths. The rare-earth series provides beautiful examples of localized excited configurations with excitation energies comparable with thermal energies. The lanthanides are known, from their magnetic properties, to exist in metallic solution with unfilled 4*f* cores virtually identical with those of free ions.[13,14] However, in some cases, notably for Yb, there exist transitions that take the impurity from one quasi-ionic state to a second via a core-to-valence transfer. In AgAu alloys, the $4f^{14}$ and $4f^{13}$ configurations cross in energy and the local moment is destroyed. Rather than ascribing this to the Kondo effect as has previously been done,[15] we believe that the anomalous transport properties that arise at the transition may plausibly be explained by spin-flip scattering that takes the impurity *from one long-lived configuration to the other* when the configurations approach degeneracy. Rigert and Flynn[13] have recently identified a transition of Ho impurities in liquid AgAl alloys in which two configurations of Ho impurities compete. It is important that these configurations are independent and compete thermally so that their relative occupation is given by a Boltzmann factor that depends on the host properties. The configuration levels are so well defined that the transition occupies precisely the range of ~0.3 eV in relative energy anticipated for thermal-equilibrium occupations of two levels crossing at the elevated temperatures of these liquid materials. Finally, for rare earths, we draw attention once more to the fact that the susceptibility of Sm impurities in metals shows unambiguous evidence of thermal redistribution among low-lying members of the inverted multiplet of levels that characterizes the 4*f* core for fixed $\vec{L}$ and $\vec{S}$.[15] The existence of these excitations is confirmed by solvent NMR measurements that also indicate that the excited levels remain independent although the *f* levels mix with band states.[14] In summary then, the rare earths provide clear illustrations of the excited quasi-ionic configurations that form the basis for our later discussion of 3*d* impurities. It may be noted that the case of trivalent Eu should provide an example in which $J=0$ in the ground state and therefore, like the nitric oxide molecule, corresponds to the case in which the local-moment character is modified beyond recognition as $T\rightarrow 0$.[16]

A second argument we wish to present in favor of high-temperature magnetic-to-nonmagnetic transitions having the chemical character of Stoner's model arises from the supposed nature of the spin-compensated state. Certainly, it is not conceivable that the weak interaction visualized in $J\vec{s}\cdot\vec{S}$ coupling could substantially modify the basic chemical state of the magnetic ion itself, for the known properties of 3*d* ions point clearly to the dominant role of spin-spin coupling in the ion core. It does seem conceivable, however, that the conduction-electron–magnetic-ion coupling could cause a moment reduction either by a diffuse spin-compensation cloud or by mixing impurity wave functions having different spin projections in such a way that a singlet state lies lowest. However, this possibility remains only when the Hartree-Fock ground state is magnetic; there appears no way in which weak interactions can produce a substantial moment on a strongly nonmagnetic impurity. Therefore, in examining the high-temperature properties of a nonmagnetic ion, we should first inquire whether or not there is reason to believe that it is magnetic in the Hartree-Fock sense before ascribing the lack of a moment to forces of a much weaker nature.

In connection with the existence of local moments at high temperature, it is worth recalling finally that their existence is, in the broad scheme, a low-temperature rather than a high-temperature phenomenon. At the highest (usually unattainable) temperatures, all local moments tend to be destroyed. The thermal excitation of more energetic band states leads inevitably in the Boltzmann limit of Fermi statistics to a decoupling of the exchange interaction that drives atomic-spin magnetism and hence to the magnetic properties of independent carriers.

Having discussed various alternative processes that can cause a magnetic-to-nonmagnetic transition at elevated temperatures, we now turn to the way in which these processes can be distinguished. First we note that in the Hartree-Fock description the susceptibility given by expressions of the form[1-3]

$$\chi \sim \chi_0/[1-JN(E_F)] \tag{1}$$

becomes singular owing to instability at the transition. This happens because the energy of the ground state is independent of magnetization for infinitesimal polarizations. An inclusion of spin excitations among the weakly configuration-dependent available energy levels is certainly necessary,[6] and these must have the effect of smoothing the singular behavior. There appears to be no question that spin fluctuations are a necessary complement to the Freidel-Anderson-type description of local moments near instability, and are distinguished by the appearance of a smooth magnetic-to-nonmagnetic transition induced by changing host properties at elevated temperatures. The existing treatments of spin fluctuations are nevertheless inadequate as they deal only with the nonmagnetic Hartree-Fock regime and then are suitable only for the description of those small fluctuations in which configurational effects are not dominant.

It is more difficult to investigate the possibility of a spin condensation on purely experimental grounds. Presumably, the detection of a delocalized spin redistribution (say, by NMR methods) would establish the model, and some efforts in this direction are discussed in the following paper. However, this is difficult to accomplish in practice because changing host properties also cause intrinsic modifications of the spin-dependent Hartree-Fock redistribution near magnetic impurities.

While studies of particular impurities at high temperatures have difficulties that make them likely to be uninformative, there remains the possibility of comparing the behavior of different magnetic impurities in similar environments. This is the approach we adopt in the present work. According to existing work[17] the Kondo temperature below which condensation takes place depends exponentially on the spin-dependent host-impurity coupling. T_K for the $3d$ impurities typically covers an enormous range for this reason. In Cu, for example, T_K for Fe is believed to be $\sim 10\,^\circ\mathrm{K}$,[7,8,17] whereas for Mn it has been said to lie at $\sim 10^{-2}\,^\circ\mathrm{K}$[18] (although the existing data do not appear to establish this unambiguously). For Co the value of T_K has been assumed to be some five orders of magnitude larger than for Mn. If we assume that the magnetic properties can be approximated in order of magnitude by some specific function of T/T_K, then it is evidently quite unlikely, in host-induced transitions at temperature T, that there will appear similar variations with host properties of the χ of different $3d$ impurities as they pass through the transition. The point is that the condition $T = T_K$ is likely to occur for different host compositions when the impurities have widely differing T_K. On the other hand, from Friedel's viewpoint, the similarity of $3d$ orbitals on different impurities makes it inevitable that they undergo similar s-d hybridization. In the presence of rather similar impurity-state densities (e.g., of Cr, Mn, and Fe), one would therefore anticipate that similarities in the host-induced magnetic-to-nonmagnetic transitions would occur.

This qualitative dissimilarity between the two models seems to provide a crude criterion with which an appeal can be made to the experimental facts. In order to assess these facts we have made the required comprehensive survey of the magnetization of V, Cr, Mn, Fe, Co, and Ni as functions of temperature through a range of liquid host metals including Cu, Zn, Ga, Ge, As, and CuZn, ZnGa, GaGe, and GeAs alloys. These results are presented in Sec. II, where it is shown that there exist striking intercorrelations among the susceptibilities of different impurities. In Sec. III we go on to describe the transitions in terms of a configurational model of spin fluctuations, in the spirit of Rigert and Flynn's discussion of excited rare-earth configurations, and attain quantitative success in describing the broad nature of these correlations.[19]

II. SUSCEPTIBILITY OF 3*d* TRANSITIONAL IMPURITIES

A. Experimental Details

Magnetic susceptibilities were measured using the Faraday method. The samples were encapsulated in fused-quartz tubes (1-mm nominal wall thickness; 2-mm walls for As alloys) that had previously been calibrated so that the capsule susceptibility could be corrected for SiO_2 magnetism and air buoyancy. In these measurements we employed a 40-kG superconducting solenoid and determined the susceptibility using a chemical balance. Absolute susceptibilities were obtained by comparison with measurements on KCl, Pb, and Pt specimens which yielded calibration constants that were mutually consistent to 2%. The samples were prepared from high-purity components, typically from 99.999%-pure host metals and 99.9%-pure transition metals. We encountered no substantial difficulties from interaction between the quartz and the samples.

B. Observed Impurity Susceptibilities

Figure 1 shows the observed susceptibility of Cr, Mn, Fe, and Co as a function of concentration c in liquid Zn at 1100 °C (V proved insoluble in Zn). In each case the susceptibility changes linearly with c to yield the molar susceptibility χ in terms of the molar host susceptibility χ_h and the molar impurity susceptibility χ_i according to

$$\chi = (1-c)\chi_h + c\chi_i \quad . \tag{2}$$

Similar results for V, Cr, Mn, Fe, and Co in liquid Ga and liquid Ge are shown in Figs. 2 and 3.

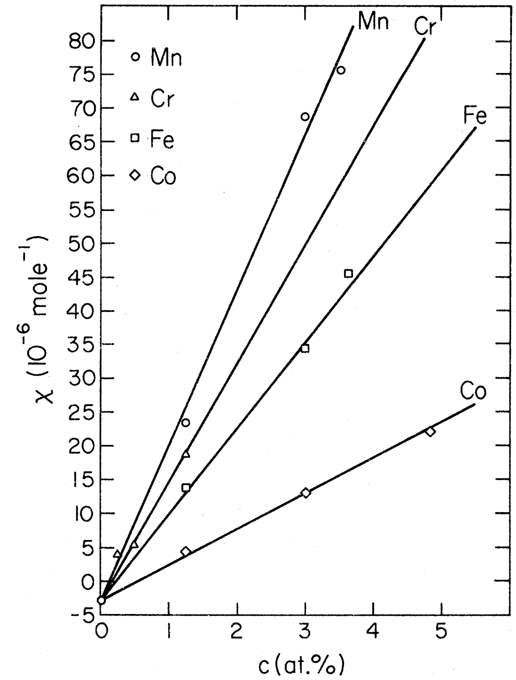

FIG. 1. Molar susceptibilities of Cr, Mn, Fe, and Co in liquid Zn at 1100 °C, shown as functions of 3*d* impurity concentration *c*.

To further verify that the concentrations used gave reasonable susceptibilities for infinite dilution, an alloy containing 9 at.% Mn was studied and found to have a susceptibility per Mn ion that deviated by 18% from the value for dilute alloys. Thus, data for $c \lesssim 3$ at.% of impurities should yield impurity susceptibilities reliable to ~5%. Relative errors in passing from one solvent to the next are likely to be much smaller than systematic errors due to the possible nonlinear variation of χ with *c*.

The observed variation with host species of χ_i for V, Cr, Mn, Fe, Co, and Ni is shown as a function of solvent electron-to-atom ratio $\mathfrak{z}$ in Fig. 4.

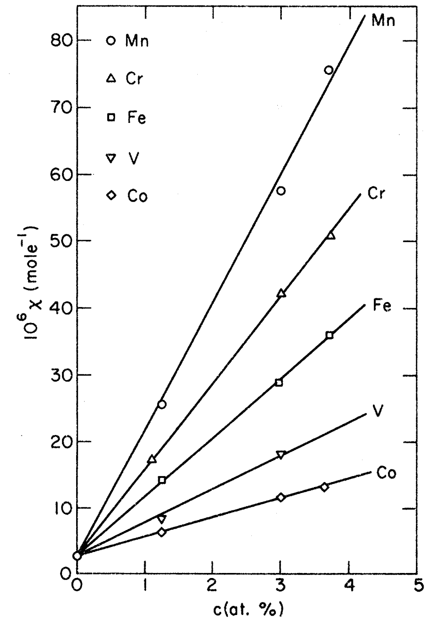

FIG. 2. Molar susceptibilities of V, Cr, Mn, Fe, and Co in liquid Ga at 1100 °C, shown as functions of 3*d* impurity concentration *c*.

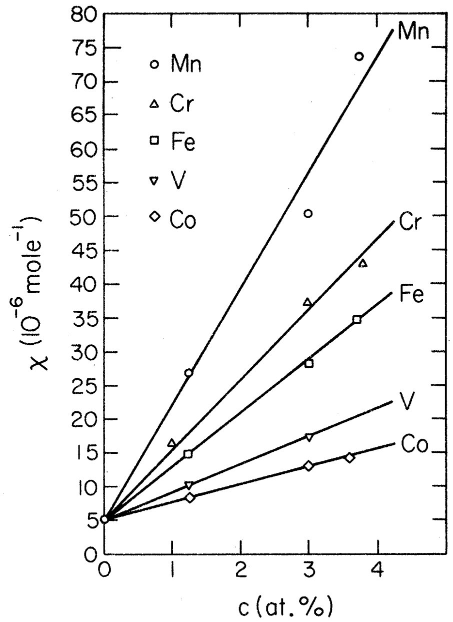

FIG. 3. Molar susceptibilities of V, Cr, Mn, Fe, and Co in liquid Ge at 1100 °C, shown as functions of 3*d* impurity concentration *c*.

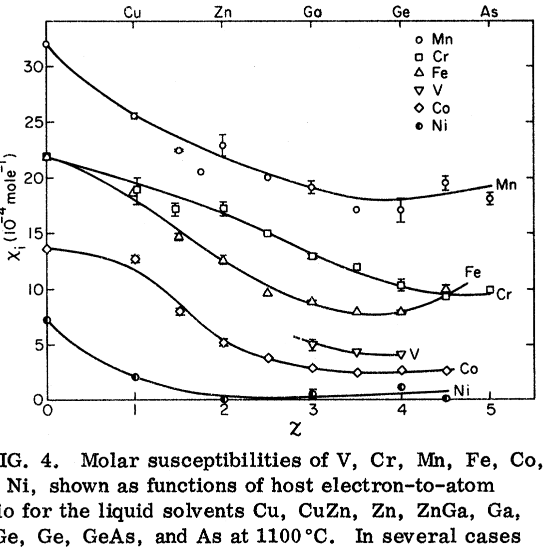

FIG. 4. Molar susceptibilities of V, Cr, Mn, Fe, Co, and Ni, shown as functions of host electron-to-atom ratio for the liquid solvents Cu, CuZn, Zn, ZnGa, Ga, GaGe, Ge, GeAs, and As at 1100 °C. In several cases the data are obtained from small extrapolations of or interpolations among data obtained by neighboring temperatures.

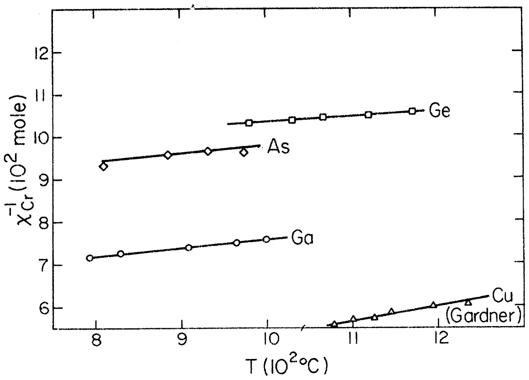

FIG. 5. χ_{Cr}^{-1} as a function of temperature in liquid Cu, Ga, Ge, and As.

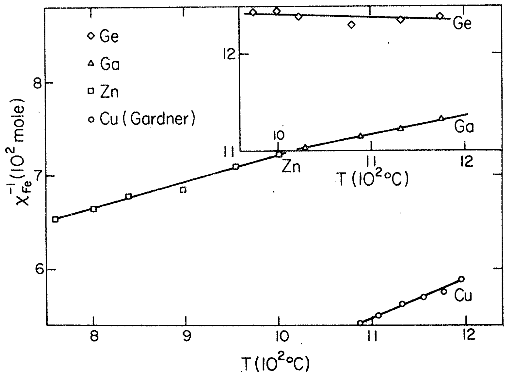

FIG. 7. χ_{Fe}^{-1} as a function of temperature in liquid Cu, Zn, Ga, and Ge.

In addition to Zn, Ga, and Ge mentioned above, the solvents employed here included 50-50 alloys of neighboring elements in the series Cu, Zn, Ga, Ge, and As. For Cr and Mn, As was also used as a solvent in the liquid at temperatures above 800 °C and a pressure of ~40 atm. Gardner and Flynn's previous data[20] for 3*d* impurities in liquid Cu are included in Fig. 4. The values for 1100 °C were in several cases obtained from small interpolations among and extrapolations of the data obtained at neighboring temperatures. The susceptibilities at 1100 °C are seen to decrease with $\mathfrak{z}$ and pass through a weak minimum at $\mathfrak{z} \simeq 4$.

Figures 5–8, respectively, show for Cr, Mn, Fe, and Co the temperature dependences of χ_i in the pure liquid metals Cu, Zn, Ga, and Ge. The additional case of As is shown for Cr in Fig. 5 and Mn in Fig. 6. The difficult case of Cr in Zn is omitted because slow solubility kinetics interfere with the measurements. In each case the data in Figs. 5–8 are extracted from raw alloy data using the temperature-dependent solvent susceptibility reported earlier.[21] In summarizing these data we note that the temperature variation of χ_i^{-1} for Cr, Mn, and Fe is in each case sensibly linear over the accessible range, as also in the temperature variation of χ_i for Co. The data often correspond to Curie-Weiss behavior with a large negative T_c, although no interpretation having this nature will be attributed to the results. The main qualitative point made evident by these results is that the local-moment character, judged from the fashioned temperature dependence, tends to die away as the susceptibility decreases through the magnetic-to-nonmagnetic transition. Thus, the *fractional* temperature variation of χ is less negative for Cr in Ge than in Cu and the absolute sus-

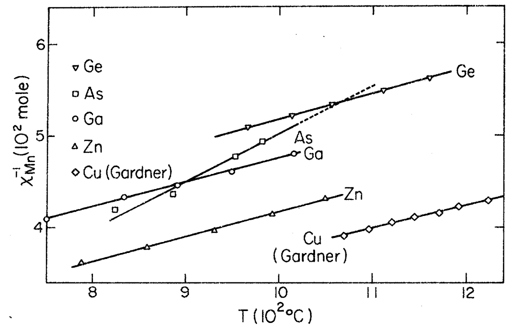

FIG. 6. χ_{Mn}^{-1} as a function of temperature in liquid Cu, Zn, Ga, Ge, and As.

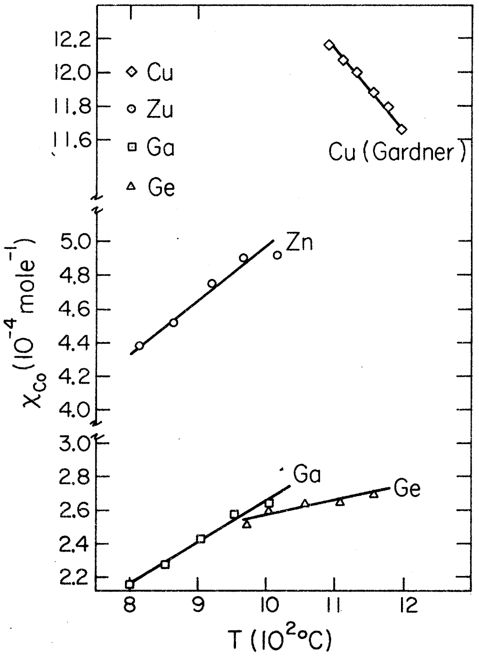

FIG. 8. χ_{Co} as a function of temperature in liquid Cu, Zn, Ga, and Ge.

ceptibility is also decreased. The same holds true for Co, Fe, and Mn (although the experimentally difficult case of Mn in As does not appear to conform). These trends of decreasing susceptibility are taken to mark the magnetic-to-nonmagnetic transition at high temperatures.

III. DISCUSSION

A. Coarse Features of Data

Figure 4 shows that the impurity susceptibilities vary rather regularly with the host valence. These results cannot be associated unambiguously with rigid-band theory or any other specific model of solvent structure. They merely indicate that the magnetism of each impurity is determined by solvent properties that vary smoothly from one host lattice to the next through the series. We show below that there is reason to believe that a single host property simultaneously determines the magnetic character of all 3*d* impurities.

It is most important that the difficult impurities undergo qualitatively similar susceptibility variations with solvent valence. Starting from Cu, an increasing complement of host band electrons reduces the impurity susceptibility monotonically, and by a factor of about 2 for $Z=4$ (Ge). Thereafter, a tendency towards increasing susceptibility is observed; a continuation through the sequence of Se, Br, Kr host lattices would doubtless restore the full ionic moment. Similar results, not previously correlated, have appeared for Mn in the series In, Sn, and Sb[22] of liquid solvents. It is clear that these effects originate from host-band-structure changes of the coarsest nature, probably dominated by modifications of bandwidth, band location, and of *s*-*d* mixing between band and impurity orbitals. We note further that the partly restored susceptibility of Mn in As is accompanied by the expected enhancement of the fractional temperature dependence, although this experimentally difficult case does not conform quantitatively to the remaining results. The correlation between the magnitude of the susceptibility and local-moment character is therefore reasonably well defined.

By far the most important correlation among the data is that the high-temperature susceptibilities of different elements are linked together by a unique relationship that holds not only for the data presented here, but also for the other solvents, according to results gathered from the literature. This correlation will be exhibited in its most striking form (including temperature dependences) in Sec. III C. It takes the following form. When the susceptibilities of any two 3*d* impurities at a given temperature are plotted against each other with the solvent as the parametric variable, then the data fall on a single curve which is particularly well defined for liquid host lattices. Presumably crystal field effects are less important in liquids so that the coarse band properties are dominant.

This correlation can most reasonably be ascribed to a certain separability of solvent and impurity properties. Each impurity has independent attributes that persist in some degree dependent only on a particular solvent property, so that as the host lattice changes, this particular property simultaneously determines the properties of all 3*d* impurities and causes unique relationships among their susceptibilities. Note that if several independent properties of the host lattice acted to fix the mean impurity pseudoatom configuration, then their independent variation from one solvent to the next would cause irregularities in the relative susceptibilities of two impurities. For this reason we are convinced that a single host property dominates the impurity structure. The net effect from an empirical viewpoint is that from a knowledge of χ_A in any solvent, one can predict χ_B, with A and B 3*d* magnetic impurities.

At the same time it is clear from Fig. 4 that the magnetic impurities Cr, Mn, Fe, and Co lose similar fractions of their magnetism in passing through the series of solvents studied in the present work. This, as noted in the Introduction, is very difficult to reconcile with current views of the spin-compensated state which predict a huge range of "Kondo temperatures" among the various impurities. It could of course be argued that T_K for each impurity changes swiftly in the observed common transition region of the impurities, but this argument may be incompatible with the observed rather broad nature of the high-temperature transitions. A much more plausible explanation is that the common trends originate in the known similarities of the *d* orbitals on different elements, and in their common overlap integral with band states, which is the central feature of the Hartree-Fock description of magnetic stability.

For this reason it is important that the susceptibilities show no sign of singular behavior near the transition; the local-moment character and the magnitude of the susceptibility both change smoothly with host properties. As mentioned in the Introduction, this must happen because thermal excitation causes an appreciable repopulation of impurities from their ground state into low-lying excited states near the instability. This repopulation must, with changing solvent properties, carry the system smoothly from the magnetic ground state to a nonmagnetic ground state. Unfortunately, the existing treatments of spin fluctuations do not appear well suited to a description in which the extremes of magnetic and nonmagnetic states appear on an equal footing.

To summarize this discussion of the coarse experimental results, we note that (a) strong corre-

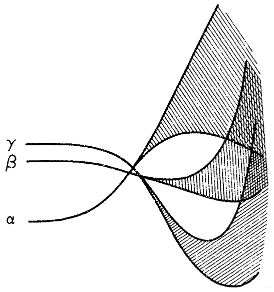

FIG. 9. Schematic diagram showing the relative shift and broadening of free-ion configurational energies α, β, and γ as the ion is exposed to host electron gases of increasing electron density.

lations among the results presented here for different impurities make the current spin-compensation description appear much less plausible than the Friedel model, and (b) the smooth behavior at the transition indicates that the Hartree-Fock model must be augmented by the inclusion of low-lying thermally excited configurations, i.e., of spin fluctuations.

B. Model of Magnetic Impurity Structure

The model of 3*d* impurity structure that we now describe is designed to accommodate two coarse experimental facts concerning these interesting systems. First, it conforms to the preceding discussion in that it represents a Hartree-Fock treatment augmented by a description of spin fluctuations that is better suited to the large spontaneous moments that emerge near the point of instability. Second, it avoids core-to-valence transfer as a mechanism for 3*d* impurity magnetization, although such effects could readily be included. The fact made evident by transport measurements is, however, that nonmagnetic 3*d* impurities, say, for example in Al, contain complements of 3*d* electrons very similar to those of the same species when magnetic in Ag.[1] This is not to say that minor degrees of average transfer do not take place; it merely indicates that the relative change in occupancy in the two 3*d* spin subbands of, e.g., Mn is very much larger than the change in the net *s*-*p* valence screen. We note in any event that the misleading concept of magnetization by core to Fermi-surface transfer, commonly employed in the literature, introduces the Fermi energy spuriously into discussions of magnetization. Impurities must remain electrically neutral over periods longer than ω_p^{-1}, with the plasma frequency ω_p typically 2×10^{16} sec^{-1}. For this reason configurations having longer lifetimes must be formed by transfer between core and valence levels, which in the self-consistent excited state may lie well below the Fermi level.

In this paper we represent spin fluctuations by means of excited pseudoatom configurations of the type (i) discussed in Sec. I. The magnetic-to-nonmagnetic transition then appears as an inversion of the multiplet of levels derived from differing values of the net ionic spin. This inversion is driven by the changing energy balance principally between exchange and kinetic energy, with changing host properties. To clarify our view of the physical processes we show in Fig. 9 the energy levels of a free ion as it is exposed to host lattices (in their ground state) of increasing electron density. The excited pseudoatom levels shift and may broaden as shown with changes of host properties. Even for the 100-eV core excitations mentioned in Sec. I, for which a wide variety of Auger and other recombination processes are possible, the widths remain much less than 1 eV so that, for example, the hole spin-orbit structure of < 1 eV remains easily visible.[9] Our belief is that for low-lying excited states of 3*d* impurities, as demonstrated for rare earths,[13,14] the levels may remain defined to better than a few hundredths of 1 eV. The result is that the configuration, in general, overlaps very little in energy, and therefore the pure ionic configuration provides the best zeroth-order description of the configuration in metals; that is, there is a negligible configuration interaction. It may not be necessary to remark that the configurational energy widths are entirely distinct from the one-electron lifetimes that measure the duration of conduction-electron–impurity collisions. The latter may be several volts wide while the configurational levels remain narrow. In effect, correlation in the impurity cell maintains the configuration over many lifetimes of the one-electron orbitals.[15]

From this approach there follows a clear picture of the ground and excited states of the host-metal–impurity complex. This is shown in Fig. 10. Each accessible configuration of the impurity core gives rise to a closely spaced set of excited levels close-

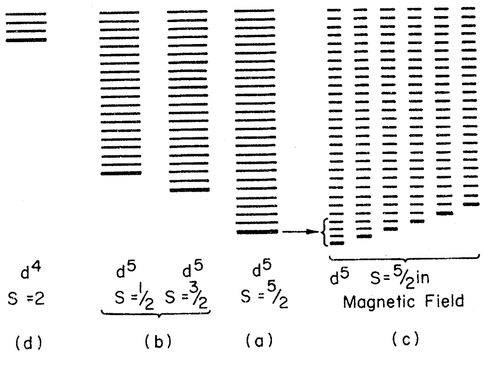

FIG. 10. Schematic diagram showing the main series of ground and excited states of Mn corresponding to core configurations obtained from (a) the core ground state by (b) excitations internal to the core, (c) magnetic field splitting, and (d) core-to-valence transfer. It is to be understood that the spacings of excited states may differ among the various series.

ly resembling the pure-host-lattice excitation spectrum (but certainly somewhat distorted). The splitting between the ground states of the series for different core configurations and the distortion of excited states each depend on the host-lattice interaction. In the present case we believe that spin-spin coupling in the core, together with kinetic-energy contributions, dominates this difference between ground states, and that the relative order of the ground-state levels in energy may change with changing host properties. This causes a transition from a magnetic to a nonmagnetic ground state.

To calculate from this model a magnetic susceptibility, we must acknowledge that the available configurations are split further by a magnetic field. This is indicated in Fig. 10(c). Now each of the separated core levels in the field gives rise to a separate series of host valence levels further distorted by the core. The susceptibility follows as

$$\chi = H^{-1}\sum_{ab} M_{ab}\, e^{-E_{ab}/kt}\Big/\sum_{ab} e^{-E_{ab}/kt} , \qquad (3)$$

in which M_{ab} is the magnetic moment and E_{ab} the energy of the entire system in the state ab having the core configuration a and valence-excitation level b. Whenever core-to-valence transfer configurations enter the problem, this susceptibility must be augmented by similar sums over such configurations.

As a primitive application of this approach, we ignore valence-to-core transfer and neglect both orbital core magnetism and spin-dependent core-to-valence coupling. The impurity and host magnetic properties then separate and the core magnetism is

$$\chi = H^{-1}\sum_{SM_S} M_S\, e^{-(E_S-M_SH)/kT}\Big/\sum_{SM_S} e^{-(E_S-M_S)/kT}$$

$$= \sum_{S} (2S+1)\,\chi(S,T)\,e^{-E_S/kT}\Big/\sum_{S} (2S+1)e^{-E_S/kT} , \qquad (4)$$

in which S is the core spin and $\chi(S, T)$ the thermal-equilibrium susceptibility of that spin system.

To proceed further we need values of E_S that are not readily available. However, a satisfactory approximation for small differences among the E_S follows from symmetry. In an isotropic system the core Hamiltonian, including all core-lattice coupling terms, can depend only on the operator $\vec{S}^2$. We therefore expand $\mathcal{H}_S(\vec{S}^2)$ in the form

$$\mathcal{H}_S(\vec{S}^2) = \alpha + \beta\vec{S}^2 + \gamma\vec{S}^4 + \cdots \qquad (5)$$

to obtain, with the neglect of terms in $\vec{S}^4$ and higher order,

$$E_S = \beta S(S+1) , \qquad (6)$$

in which the irrelevant constant α is omitted. This is the crystal analog of the well-known atomic dependence of E_J on J. Our result for the susceptibility now takes the form

$$\chi(\beta, T) = \sum_{S=S_{\min}}^{S_{\max}} (2S+1)\chi(S,T)e^{-\beta S(S+1)/kT} \times\left(\sum_{S=S_{\min}}^{S_{\max}} (2S+1)e^{-\beta S(S+1)/kT}\right)^{-1} . \qquad (7)$$

Here $S_{\max}$ and $S_{\min}$ are, respectively, the maximum and minimum core spins permitted by the exclusion principle. We stress here that β contains all details of the host-impurity spin interaction and therefore is, in general, both temperature and host-lattice dependent.

To complete this approximate analysis in a neat form, we evaluate $\chi(\beta, T)$ in the high-temperature approximation by writing for the Brillouin function

$$\chi(S, T) \to g^2\mu_B^2 S(S+1)/3kT \qquad (8)$$

and taking S as a continuous variable from 0 to S_m. Then[19]

$$\chi(\beta, T) = \frac{g^2\mu_B^2}{3\beta} - \frac{g^2\mu_B^2 S_m(S_m+1)}{3kT\{\exp[\beta S_m(S_m+1)/kT]-1\}} . \qquad (9)$$

This susceptibility is depicted as a function of β and T in Figs. 11 and 12. Figure 11 shows the susceptibility as a function of β for various temperatures and $S_m = \frac{5}{2}$ (e.g., Mn). There is a smooth transition from local-moment behavior for $-\beta$ large (when S_m alone is occupied) to temperature-independent magnetism for β large. Thus, inclusion of excited configurations smooths the transi-

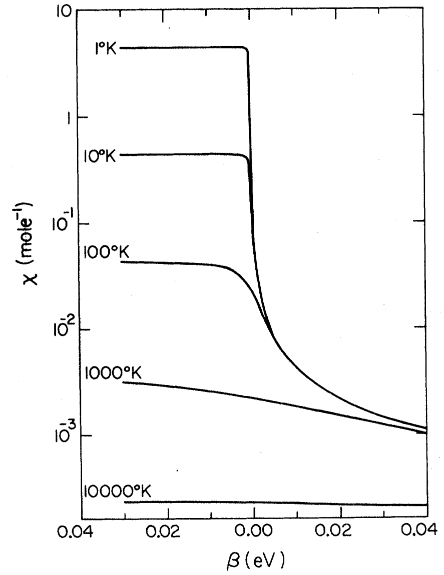

FIG. 11. Susceptibility of Mn as a function of β(eV), according to Eq. (9), shown for various temperatures.

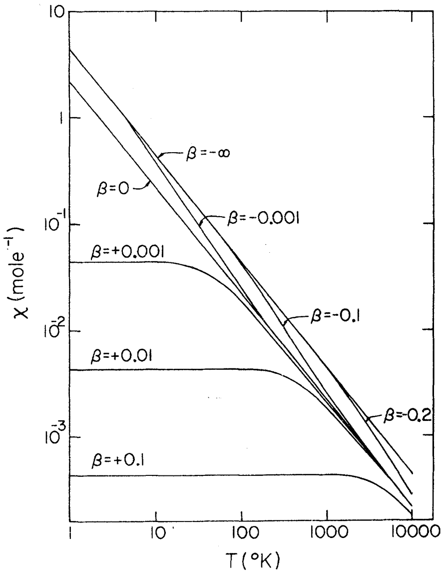

FIG. 12. Susceptibility of Mn as a function of temperature, according to Eq. (9), shown for various values of β(eV).

tion in a physically realistic manner. Figure 12 shows how the susceptibility varies with temperature for various β and $S_m = \frac{5}{2}$. At the highest temperatures the susceptibility is half that for the S_m configuration, while at lower temperatures and $\beta < 0$, it corresponds to $S = S_m$. For $\beta > 0$ there occurs with decreasing temperature a transition from Curie-law behavior to enhanced polarizability reminiscent of properties frequently associated with the Kondo effect. The transition has a physical character analogous to that of Eu^{+++} in salts.

The crude approximations made in deriving Eq. (9) can obviously be improved to any required degree. There remain, however, certain physical points that bear further comment. These concern the coupling between the core spin and the spins of the remaining conduction electrons, and the nature of the low-spin configuration. It is to a brief discussion of these properties that we now turn.

Consider then the spin $\vec{\mathcal{S}}$ of the entire piece of metal, neglecting core spin $\vec{S}$ and neglecting also any coupling between $\vec{\mathcal{S}}$ and $\vec{S}$. The Hamiltonian must again be isotopic and therefore depends only on $\vec{\mathcal{S}}^2$. Thus $\mathcal{H}(\vec{\mathcal{S}}^2) = \alpha_0 + \beta_0 \vec{\mathcal{S}}^2 + \gamma_0 \vec{\mathcal{S}}^4 + \cdots$, and the energy levels are given by

$$E_{\mathcal{S}} = \beta_0 \mathcal{S}(\mathcal{S}+1) \quad , \tag{10}$$

as in Eq. (6). Of course, $\beta_0 \ll \beta$ because the entire solid has an enormous polarizability by comparison with the local spin. Moreover, the high-temperature approximation never holds for the large values of $\vec{\mathcal{S}}$ that are relevant to the metal. The correct susceptibility is obtained by the now completely valid procedure of replacing sums over $\mathcal{S}$ and $\mathcal{S}_z$ by integrals. We find

$$\chi = H^{-1} \frac{\int_0^\infty \int_{-\mathcal{S}}^{\mathcal{S}} g\mu_B \mathcal{S}_z \exp\{-[\beta_0 \mathcal{S}(\mathcal{S}+1) - g\mu_B \mathcal{S}_z H]/kT\}\, d\mathcal{S}\, d\mathcal{S}_z}{\int_0^\infty \int_{-\mathcal{S}}^{\mathcal{S}} \exp\{-[\beta_0 \; (\mathcal{S}+1) - g\mu_B \mathcal{S}_z H]/kT\}\, d\mathcal{S}\, d\mathcal{S}_z} \quad , \tag{11}$$

which leads to

$$\chi = g^2 \mu_B^2 / 2\beta_0 \tag{12}$$

in both the high-field and low-field limits. This differs from the leading term of Eq. (9) by a numerical factor of $\frac{3}{2}$ because the high-temperature limit invoked for Eq. (9) is not valid for the bulk metal. The large values of $\mathcal{S}$ in the polarized crystal lead inevitably to the appearance of only those states with $\mathcal{S}_z \simeq \mathcal{S}$, so that the host-lattice spins are predominantly oriented along H as in the simple two-spin band treatment of Pauli susceptibility. A comparison with the usual exchange-enhanced susceptibility of the one-electron model[1-3]

$$\chi_P = \mu^2 N(E_F)/[1 - JN(E_F)] \tag{13}$$

shows that

$$\beta_0 = 2[1 - JN(E_F)]/N(E_F) \; . \tag{14}$$

Here $[1 - JN(E_F)]^{-1}$ is the enhancement factor with $N(E_F)$ the density of one-electron levels at E_F. We do *not* necessarily ascribe a similar meaning to β of Eq. (6) in terms of the local density of impurity d states at E_F and a local enhancement factor for spin polarization. The fact is that for such substantial fractional changes in S the local density of states may change appreciably.

There will, in general, exist a coupling between the host- and impurity-spin systems. In an isotopic system this coupling must to the lowest order take the form $\mathcal{H} = \kappa_S \vec{S} \cdot \vec{\mathcal{S}}$. It is important to note that, for a one-electron description of the host lattice, this form of interaction with κ_S constant has no significance for states remote from the Fermi energy. For the small range of one-electron energies involved in thermal redistribution and polarization phenomena, it nevertheless seems plausible that κ may be independent of the precise excited state of the host electrons to which $\vec{\mathcal{S}}$ pertains. However, there is no reason to suppose that κ is independent of the impurity spin S, and the κ_S for different S must in general differ. For example, configurations corresponding to different S may have differing local state densities at E_F.

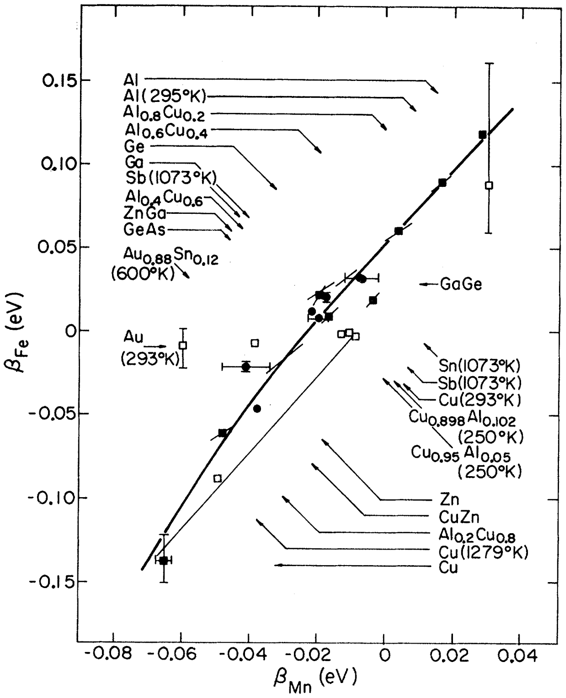

FIG. 13. Variation of β_{Fe} with β_{Mn} among various solvents. Full points mark liquid host lattices and open points, solid lattices.

An interaction of the form $\kappa_S \vec{S} \cdot \vec{s}$, with $\vec{s} = \sum_i s_i$, has two well-known effects. First the average polarizations $\langle S_z \rangle$ and $\langle s_z \rangle$ induced by an external field are modified. The change in $\langle s_z \rangle$ may be particularly large because the host density and polarizability are so large ($\beta_0 \ll \beta$). There results a change in the spin polarization caused by core reorientation in the applied field, and the local moment is, in effect, modified. Second, the interaction causes compensating spin-flips in the host- and impurity-spin systems. The impurity spin may be scattered between different M_S or between different S, and scattering between nearly degenerate configurations differing by core-to-valence transfer may, presumably, also occur. It is the latter process to which we allude in our earlier comments concerning Yb in AgAu alloys.

The inclusion of spin-dependent host-impurity coupling draws attention to a difficulty in the treatment of low-spin configurations. In addition to transitions that take the composite system S, s from one configuration to a second, there undoubtedly exist fluctuations inside the wave functions themselves. Spin fluctuations (paramagnons) in highly polarizable materials have been observed as independent excitations that contribute substantially to the thermal and transport properties of the host lattice.[23] During band electron-impurity collisions the memory of the initial configuration must be very weak for ions in low-spin configurations (say, Mn with $S = \frac{1}{2}$) because $\Delta S_z = 1$ reverses the magnetization. This is not the case for Mn with $S = \frac{5}{2}$ because the $S = \frac{3}{2}$ configuration may be far removed in energy, and only transitions with $\Delta S_z = 1$ occur. There must undoubtedly arise a limit of strong impurity-host coupling in which fluctuations of a small impurity spin appear as an intrinsic part of the ground-state wave function rather than as the occupation of alternative values of S_z. This limit is, for example, reached by Al impurities in Mg. Our crude derivation of Eq. (9), while perhaps phenomenologically acceptable, evades this interesting conceptual distinction. Thus, Eqs. (9) and (12) provide additive enhanced polarizabilities whereas in principle the impurity merely modifies β_0 in this extreme limit. Our treatment employs a suitable local analog of paramagnons rather than a polarizability that may, in this limit, be more directly associated with the spectrum of one-electron levels.

In concluding this description of the model we note that a simple relationship connects the total energy $\langle E_S \rangle$ and the susceptibility $\langle \chi_S \rangle$ originating in core excitations. Using Eqs. (6) and (8) we find

$$\langle E_S \rangle = (3kT\beta / g^2 \mu_B^2) \langle \chi_S \rangle \; . \qquad (15)$$

C. Analysis of Susceptibility Data

We now apply the model presented in Sec. III B to an analysis of the high-temperature susceptibilities reported in Sec. II and other data collected from the literature. The sources of the data are cited in Ref. 24. For lack of reliable information concerning orbital-impurity magnetism and host-impurity coupling in these latttices, we are obliged to simplify the analysis. In what follows we assume that spin magnetism predominates and that the coupling between $\vec{S}$ and $\vec{s}$ introduces only minor errors. Core-to-valence transfer is also ignored, and the analysis proceeds directly from Eq. (9). The observed χ_i for $T > 270$ °K, after minor corrections for core diamagnetism, are used to solve Eq. (9) for β. In each case the chosen S_m is appropriate for the divalent ion, i.e., for V, $S_m = \frac{3}{2}$; Cr, $S_m = 2$; Mn, $S_m = \frac{5}{2}$; Fe, $S_m = 2$; Co, $S_m = \frac{3}{2}$; Ni, $S_m = 1$. The values of β_i so deduced are shown in Figs. 13–20 as plots of β for one impurity against β for a second impurity, with host properties providing the parametric link between the two variables. In those cases for which reliable temperature dependences of the susceptibility are available, the loci of points traced by the β with varying temperature are indicated by faint lines. To assess the possibility of significant core-to-valence charge transfer, we also indicate in Figs. 18–20 the variations with solvent species of β_{Cr} for a hypothesized $S_m = \frac{5}{2}$ configuration.

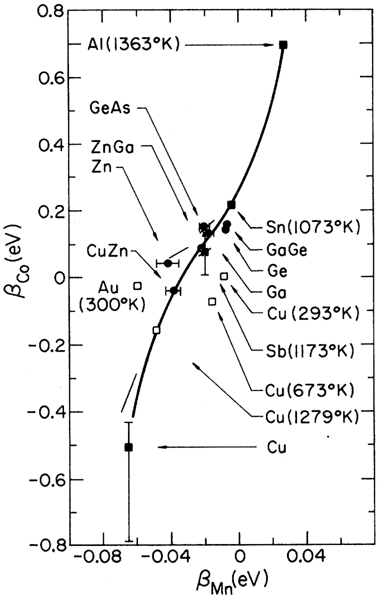

FIG. 14. Variation of β_{Co} with β_{Mn} among various solvents. Full points mark liquid host lattices and open points, solid lattices.

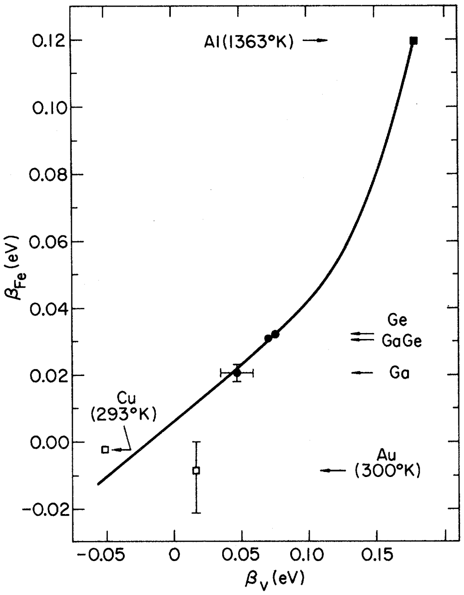

FIG. 16. Variation of β_{Fe} with β_V among various solvents. Full points mark liquid host lattices and open points, solid lattices.

It is abundantly clear from these results that there exist rather well-defined relationships among the β for different impurities as the host lattice changes. Points derived from chemically distinct solvents at different temperatures and the observed temperature dependences in any solvent all tend to lie on the same unique lines. These lines are particularly well defined for the case of liquid solvents (full points). Not only do these relationships exist, but there also exist deeper correlations among the β. Most notable is the fact that the β for different impurities pass through $\beta = 0$ almost simultaneously as the solvent is varied. Moreover, those im-

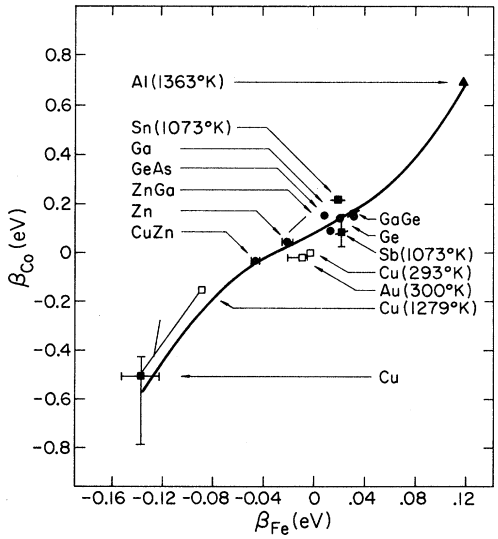

FIG. 15. Variation of β_{Co} with β_{Fe} among various solvents. Full points mark liquid host lattices and open points, solid lattices.

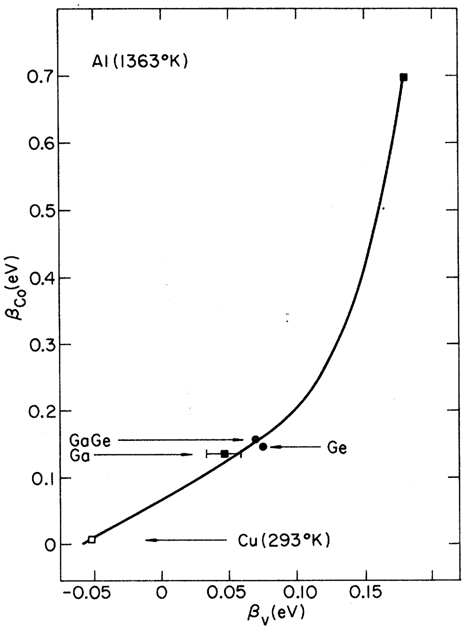

FIG. 17. Variation of β_{Co} with β_V among various solvents. Full points mark liquid host lattices and open points, solid lattices.

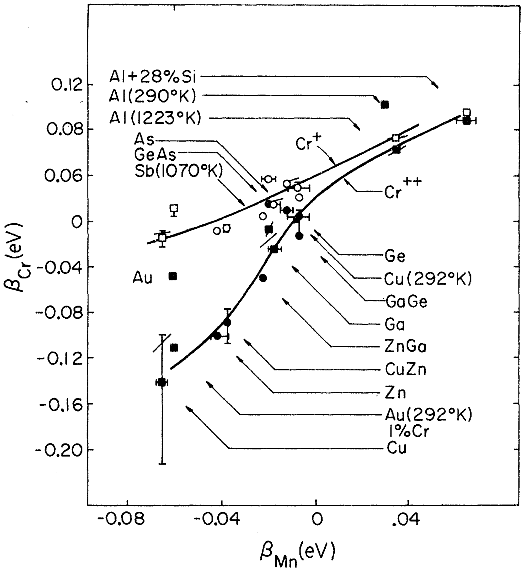

FIG. 18. Variation of β_{Cr} with β_{Mn} among various solvents. Full points represent results for the hypothesized d^4 configuration of Cr, and open points are for the d^5 configuration. Circles and squares, respectively, denote liquid and solid solvents.

purities with smaller S_m have large β indicating that their energy varies more rapidly with S. The curves involving impurities with S_m small tend to have a sigmoidal character that indicates a nonlinear dependence of the β on the host properties. We note that curves for Cr^{++} conform much better to these regularities than Cr^{+}, and therefore we neglect valence-to-core transfer in what follows.

These results provide strong support for our analysis of 3*d* impurity structure. If the data were derived only from results obtained at a single temperature, then the correlations would indicate no more than that the susceptibilities of the different impurities are uniquely interrelated. However, the data do in fact pertain to a variety of temperatures, and the β are derived using Eq. (9). For this reason the existence of unique relationships among the different β supports our analysis of the impurity structure and in particular our approach through the concept of excited impurity pseudoatoms.

The mutual consistency of the data is further illustrated by the ordering of points along the lines of *independent* systems. For the β-β graphs of Cr-Mn and of Fe-Co the solvents lie in the following orders (solid solvents in parentheses):

Cr-Mn: Cu, (Au), Zn, CuZn, ZnGa, Ga,
Sb, GaGe, GeAs, (Cu), As, Ge, Al, (Al) ;

Fe-Co: Cu, CuZn, (Au), (Cu), Zn, ZnGa,
Ga, Sb, GaAs, Ge, GaGe, Sn, Al .

When it is realized that the ordering often lies within the experimental uncertainties of the measured susceptibilities, these results indicate the spectacular degree to which the properties of different impurities are interrelated.

We deduce from these results that the magnetism

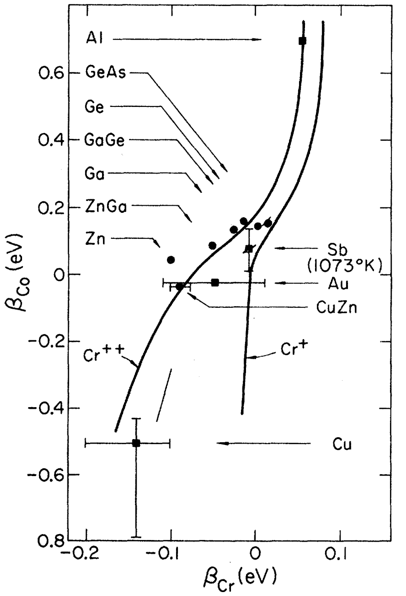

FIG. 19. Variation of β_{Co} with β_{Cr} among various solvents. The notation is indicated in the caption of Fig. 18.

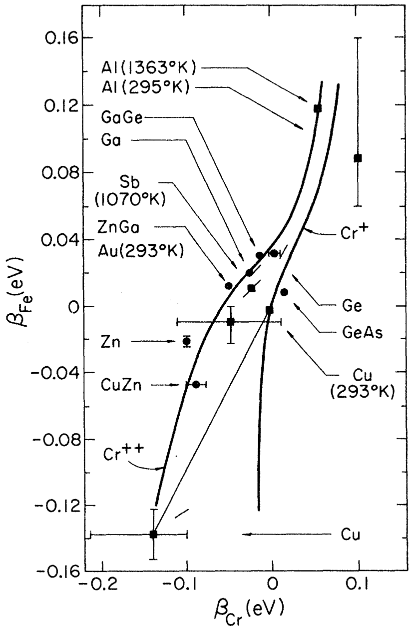

FIG. 20. Variation of β_{Fe} with β_{Cr} among various solvents. The notation is indicated in the caption of Fig. 18.

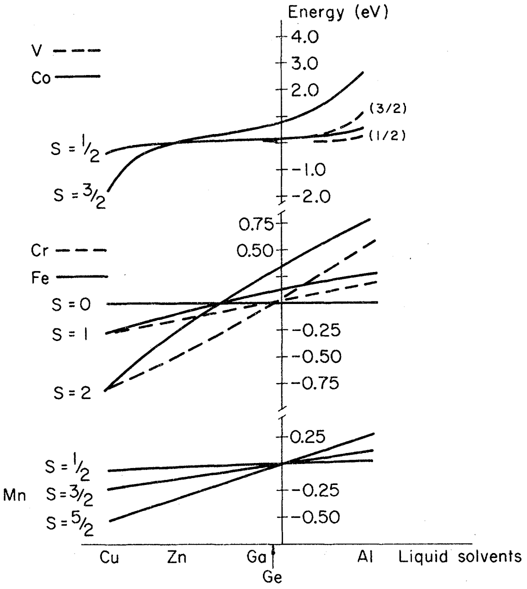

FIG. 21. Variation of the configurational levels of V, Cr, Mn, Fe, and Co with host lattice, as indicated by the results shown in Figs. 13–20.

of $3d$ impurities in simple metallic solvents is determined by a single solvent property. Presumably this single property simultaneously determines all the β for different impurities, and gives rise to the observed relationship among the β. If several unrelated solvent properties were important, they could not be expected to be reproduced from one solvent to the next, and the relationships among the β would become blurred. We have verified that the relevant property is not simply the electron-to-atom ratio or the (free-electron) Fermi energy. It seems likely that the host property of interest may be the d-like character of the host conduction band. This quantity may determine the magnetic polarizability by fixing the one-electron lifetimes of the impurity d orbitals, and in this way controlling the kinetic-energy change during polarization.[1] The exchange energy that balances this kinetic energy may be less sensitive to host properties. The relations among the β of different impurities thus follow in a straightforward way from the similarity of the d orbitals of the various $3d$ transitional elements.

Figure 21 shows the configurational levels as a function of solvent, as deduced from the data of Figs. 13–20. Since for Mn the β vary least and are best known, the ordering of points has been derived from smoothed results for Mn. It is interesting that although configuration interactions must, in principle, occur when the levels are degenerate near $\beta = 0$, the data show no signs of anomalous behavior there. This may indicate that the configurational levels are indeed very narrow and remain sensibly distinct under all accessible conditions.

There remain several minor points to be made concerning Figs. 13–20. The values of β_i do not pass through zero for precisely the same solvent. When $\beta_{\text{Mn}} = 0$ eV, β_i are $\beta_{\text{V}} = 0.026$ eV, $\beta_{\text{Cr}} = 0.005$ eV, $\beta_{\text{Mn}} = 0.000$ eV, $\beta_{\text{Fe}} = 0.024$ eV, and $\beta_{\text{Co}} = 0.036$ eV. These differences are notably systematic and correlate strongly with the known magnetic tendencies of these elements. However, the origin of the minor displacements remains obscure. The slopes of the β-β graphs near $\beta = 0$ show similar effects. Their ratios are $5 : 1.6 : 1 : 2.3 : 6.3$ for V, Cr, Mn, Fe, and Co, respectively. It is possible that these facts are connected together through minor errors introduced by the approximations made in deriving Eq. (9).

According to the assembled evidence, copper is an unusual host material in which temperature changes cause the β to vary over wide ranges, although in good conformity with the β-β lines. The origin of this feature is not clear, and similar results for other noble-metal solvents at high temperature are still wanting. However, it is noteworthy that the Knight shift in Cu exhibits similarly large variations that are also divided almost equally between the melting transition and the temperature range between room temperature and the melting point.[25] Evidently the Cu host has substantially temperature-dependent electronic properties. It is therefore of some concern to note that the β in solid Cu all approach zero at low temperatures. Whether this happens fortuitously or through some specific host-impurity coupling we are unable to say. However, the fact is that according to the present approach the different configurations of $3d$ impurities in Cu do approach degeneracy at lower temperatures. These effects could lead at low temperatures to the unusual magnetic properties indicated in Figs. 11 and 12 for $\beta \sim 0$ and also to the anomalous transport properties to which we make mention above for the particular case of Yb in the AgAu system.

We note finally that the analysis of $3d$ impurity magnetism presented in this section has of necessity neglected the additional effects of orbital magnetism and of $\vec{S} \cdot \vec{s}$ polarization of the electron gas. While these omissions cannot be justified in detail, it seems likely that the dominant high-temperature effects have been identified correctly. Further remarks concerning the orbital and valence magnetism of $3d$ impurities are deferred to the following paper.

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