

***AuV* and *AlMn*: Kondo Systems or Localized Spin-Fluctuation Systems?**

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The predictions of the localized spin-fluctuation model and those of a theory of the low-temperature behavior of the multiorbital Anderson model we have recently developed are compared with respect to both the bulk properties (resistivity, specific heat, and magnetic susceptibility) and the microscopic properties (impurity nuclear-resonance shift and relaxation rate) for the dilute magnetic alloys *AuV* and *AlMn*.

Almost all models which have been proposed to describe the dilute magnetic alloy system may be regarded as special cases of the Anderson model.¹ For example, the *s-d* exchange model² may, by virtue of the Schrieffer-Wolff transformation,³ be regarded as corresponding to the case $|\epsilon_d|, U \gg \Delta$, where ϵ_d is the resonance energy, U is the intra-atomic Coulomb repulsion, and Δ is the resonance half-width; we shall refer to this limit of the Anderson model as the Kondo model. On the other extreme, the localized spin-fluctuation (LSF) model⁴ corresponds to the limit $|\epsilon_d| \ll \Delta$; we shall regard the studies of the Wolff model by Suhl and co-workers,⁵ despite their more ambitious attempt to treat the Coulomb interaction between all electrons on an equal footing, to be of this latter class insofar as the resonance level has been taken to be at the Fermi level in all the published work.

Since the relative magnitudes of the parameters U , ϵ_d , and Δ play such a fundamental role in all the models, the determination of these parameters from experiment is of great interest. As these quantities are not directly measured, however (unless optical or photoemission studies are undertaken), one must infer the value of these parameters from the theoretical results for the various models. Here one is confronted with the rather remarkable result obtained by Rivier and Zuckermann⁴—the LSF and the Kondo models would appear to be indistinguishable with regard to the predicted behavior of the system. Although we feel this result deserves a more detailed discussion than may be found in the literature, it is not our intention in this Letter to dispute this claim. Rather, we accept at face value all the results obtained by Rivier and Zuckermann (and others) from the LSF model and yet suggest that the predictions of the two models *are* distinguishable, provided we confine our attention to $T \ll T_K$ and take into account the orbital degeneracy present in the real alloys studied.

Before embarking on the detailed comparison

between the predictions of the two models, it is worth noting the different mechanisms proposed in dealing with the absence of orbital paramagnetism. In the case of the LSF model, which is taken to be nonmagnetic in the Hartree-Fock sense, the absence of orbital paramagnetism is accounted for by the argument first given by Anderson¹: The spin-enhancement factor σ_d is considered to be much greater than the orbital-enhancement factor σ_0 because of the different dependence of σ_d and σ_0 on J , the exchange integral. In the case of the Kondo model, however, the system is magnetic in the Hartree-Fock sense and the orbital paramagnetism can only be quenched by the existence of crystal fields of sufficient asymmetry. It should therefore not be surprising that there may exist qualitative differences between the two models when orbital degeneracy is considered.

In order to point out these differences, it is useful to consider a specific example in detail. We choose to examine the dilute magnetic alloy *AuV* for which there exists a fairly extensive body of information. In view of the many parameters entering the theory, the numerical analysis presented here should in no way be regarded as definitive; our object is merely to illustrate the different types of reasoning involved in the two cases and to suggest the importance of certain experiments by which the numerical arguments may be strengthened.

The reasons for supposing the *AuV* system to be an LSF system are these: First, the observed zero-temperature resistivity⁶ ($15 \mu\Omega \text{ cm/at.}\%$) is not very different from that obtained by the Friedel formula,

$$R(0)/c = 5\rho_0 \sin^2(\frac{1}{10}\pi n_d) \cong 12 \mu\Omega \text{ cm/at.}\%, \quad (1)$$

where c is the concentration of impurities, ρ_0 is the "unitarity"-limit resistivity ($4\pi/ne^2k_F$), and n_d is the number of d electrons on the impurity, which we take to be three for *AuV*. Second, in the case $\sigma_d \gg \sigma_0$, the specific heat is given in

terms of the zero-temperature susceptibility⁷:

$$\begin{aligned} \Delta C_V/T[\Delta\chi(H=0)]_{T=0} &= \frac{1}{10}\pi^2(2k_B/g\mu_B)^2 \\ &\cong (k_B/\mu_B)^2, \end{aligned} \quad (2)$$

in fair agreement with

$$\Delta C_V/T[\Delta\chi(0)]_{T=0} \cong 0.65(k_B/\mu_B)^2, \quad (3)$$

obtained from the measured values of the specific heat,⁸ $\gamma = 63$ mJ/mole °K², and susceptibility,⁶ $\Delta\chi(0)/c = 47 \times 10^{-4}$ emu/mole.

The static magnetic susceptibility is observed to be, at sufficiently high T , of the form⁶

$$\Delta\chi(0)/c = \theta/(T + T_K) + \varphi, \quad (4)$$

where $T_K = 290^\circ\text{K}$. However, for $T \ll T_K$, the susceptibility was recently found by Van Dam and Gubbens to be of the form⁹

$$\Delta\chi(0)/c = [\Delta\chi(0)/c]_{T=0}(1 - AT^2), \quad (5)$$

where $A = 6 \times 10^{-5}$ (if T is given in degrees Kelvin) for a 0.30-at.% alloy and 3.8×10^{-5} for a 0.15-at.% alloy. Although such a quadratic dependence was predicted for the LSF model by Rivier and Zuckermann, the factor $1 - 3n^2$ appearing in the coefficient of their T^2 term [Eq. (13) of Ref. 4] may be written as $1 - 3 \cot^2(\frac{1}{10}\pi n_d) = [1 - 4 \cos^2(\frac{1}{10}\pi n_d)] \sin^{-2}(\frac{1}{10}\pi n_d)$, making use of the Hartree-Fock result $\frac{1}{10}\pi n_d = \cot^{-1}(\epsilon_d/\Delta)$. For $n_d = 3$ this factor is negative, so that they find an *increase* in $\Delta\chi$ with T^2 .

Although we might expect a similar factor to appear in the expression for the T^2 term in the resistivity, the expression given in their Letter [Eq. (6) of Ref. 4] is in fact independent of ϵ_d (and thus n_d) and therefore predicts a decrease of R with T^2 as observed.

The LSF model also yields an unambiguous prediction for the spin and orbital contributions to the impurity nuclear-resonance shift and relaxation rate. From the Korringa-like equations valid in this model¹⁰

$$K_o^2(T_1T)_o = 10s, \quad K_d^2(T_1T)_d = 5s, \quad (6)$$

where $s = (\gamma_e/\gamma_n)^2 \hbar / 4\pi k_B$, we obtain from the observed Knight shift ($K = -1.5\%$) and relaxation time ($T_1T = 17$ msec °K)¹¹ the assignment

$$K_o = 2.1\%, \quad K_d = -3.6\%, \quad (7)$$

if we set $g = 2$ (see below). The validity of this assignment is best tested by a study of the temperature dependence of the Knight shift, as we may suppose the orbital contribution to be relatively temperature independent. Although, as we

shall see below, a similar assignment is predicted for AuV for the Kondo model, such an experiment would in general be very valuable in answering the question posed in the title of this Letter.

Let us now turn to a description of the alloy as a Kondo system. We shall work with the results of a theory of the low-temperature behavior of the Kondo system we have recently developed.¹² The system is characterized by a total spin S , which we assume to be $\frac{1}{2}n_d$ for $0 \leq n_d \leq 5$ and $\frac{1}{2}(10 - n_d)$ for $5 \leq n_d \leq 10$. Thus for AuV we take $S = \frac{3}{2}$. We also assume the existence of a cubic crystal field characterized by the energy difference $E(T_2) - E(A_2) = 10D$ (see Fig. 1). The theory is similar to that used by Migdal¹³ to discuss the critical behavior of a Bose liquid and suffers from the same defect—although we obtain relations between the physical properties (scaling laws), we cannot obtain the coefficients or the energy scale $k_B T_o$ [$T_K = 0.67(S+1)T_o$]. If we assume the vanishing of the linear term (in T) in the low-temperature expansion of the static susceptibility, however, we may obtain the coefficient of the quadratic term:

$$\Delta\chi(0)/c = [\Delta\chi(0)/c]_{T=0} [1 - 2(T/T_K)^2]. \quad (8)$$

From Van Dam and Gubbens's results, we find from Eq. (8) that $T_K = 185^\circ\text{K}$ for the 0.30-at.% alloy and $T_K = 230^\circ\text{K}$ for the 0.15-at.% alloy. It is not unreasonable to suppose that in the limit of infinite dilution one would obtain $T_K = 290^\circ\text{K}$ as observed at higher temperatures, and we shall use this value in the remainder of the analysis.

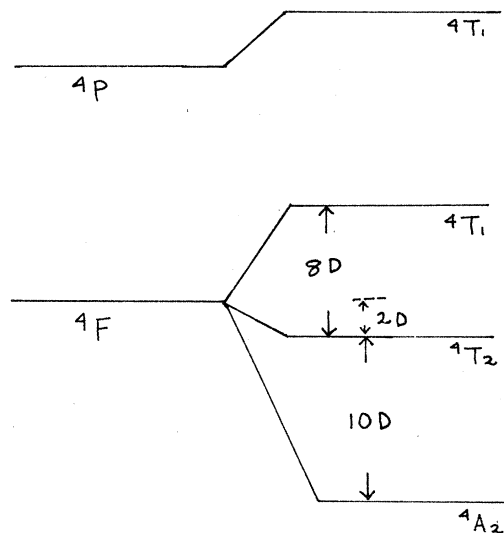


FIG. 1. Energy-level diagram in the case of weak octahedral crystal field.

Having assumed a quadratic dependence of the susceptibility upon T , we also find that for $T \ll T_0$

$$R(T)/c = 2S\rho_0\eta[1 - \alpha(T/T_0)^2]. \quad (9)$$

The coefficients α and η cannot be obtained from the theory; they are, however, expected to be of order unity. Star¹⁴ has measured the coefficient of the T^2 term; using his result and the value $T_0 = 175^\circ\text{K}$ corresponding to $T_K = 290^\circ\text{K}$, we find $\alpha = 0.5$. We might note that the LSF model would yield, from Eqs. (6) and (8) of Ref. 4, a value $\alpha = 0.35$. The value of η is more difficult to obtain as there is present an unknown amount of s -wave, p -wave, etc. scattering. In order to introduce a minimum number of parameters we shall suppose $\eta = 1$. The parameters α and η also enter into the expression for the specific heat:

$$\begin{aligned} \Delta C_V/cT &= 2S\eta(0.4 + 0.25\alpha)R/T_0 \\ &\cong 71 \text{ mJ/mole } ^\circ\text{K}^2, \end{aligned} \quad (10)$$

if we use the values for these parameters noted above. This value is in good agreement with the observed value; we may improve the agreement by allowing for an $\eta < 1$, but such refinement is not required for the purpose of our discussion.

The orbital and spin magnetic susceptibilities are given, for $T = 0$, by

$$\begin{aligned} \text{Re}\chi_0(0) &\equiv \varphi = \left[\frac{50}{16}(10D)^{-1} + \frac{30}{16}(18D)^{-1} \right] \mu_B^2, \\ \text{Re}\chi_d(0) &= (g\mu_B)^2 S(S+1)/3k_B T_K, \end{aligned} \quad (11)$$

and by

$$\begin{aligned} \text{Im}\chi_d(\omega)/\hbar\omega &\xrightarrow{\omega \rightarrow 0} (g\mu_B)^2 2S(S+1)^2/(3k_B T_K)^2, \\ \text{Im}\chi_0(\omega)/\hbar\omega &\xrightarrow{\omega \rightarrow 0} \left[\frac{50}{16}(10D)^{-2} + \frac{30}{16}(18D)^{-2} \right] \\ &\quad \times \eta\mu_B^2 U^2 (\epsilon_d + U)^{-2}/\pi, \end{aligned} \quad (12)$$

thus giving rise to the Korringa-like relations

$$\begin{aligned} K_0^2(T_1 T)_0 &= 7.5(\epsilon_d + U)^2 s/U^2, \\ K_d^2(T_1 T)_d &= \pi S s, \end{aligned} \quad (13)$$

if we set $g = 2$ and $\eta = 1$ as noted. For $S = \frac{3}{2}$, the spin Korringa product is very close to the LSF value. In order to proceed further, the ratio $(\epsilon_d + U)/U$ is required. If the temperature dependence of the impurity Knight shift were known, we could use Eq. (13) to determine this quantity which, as we have noted, is of fundamental importance. At the present time we can only assume a value for this ratio and study the consequences of our choice. Let us reason as follows: In Ref. 10 it was found that for CuNi , $U \sim 6 \text{ eV}$ ($= U + 5J$ in the notation of Ref. 10). If we de-

crease this value in proportion to the ratio of the free-atom values for V and Ni , we find $U = 4 \text{ eV}$. From the measured value $|J\rho| = 0.2$ found by Kume, the possible values of Δ and ϵ_d are thus constrained by the Schrieffer-Wolff transformation³

$$J\rho = \Delta U/2S\pi\epsilon_d(\epsilon_d + U). \quad (14)$$

A reasonable, but by no means unique, choice might be $\Delta = 0.6 \text{ eV}$ and $|\epsilon_d| = 0.4 \text{ eV}$. In the case of CuNi , Δ was found to be 0.25 eV . The larger value we obtain for AuV is consistent with the expansion of the wave function in this alloy, as noted in Ref. 11. With the above choice of U and ϵ_d we find $(\epsilon_d + U)/U = 0.9$. Setting $g = 2$ (see below), we find from the observed low-temperature Knight shift and relaxation rate an almost identical assignment as given in Eq. (7). This is a somewhat fortuitous result—for MoCo , where we may suppose $S = 1$, we would obtain a significant difference. Even for AuV , a test of the assignment of Eq. (7) would be of great interest, since the specific value of the Korringa product for the Kondo system is intimately related to the coefficient of the (assumed zero) coefficient of the linear term in the low-temperature expansion of the susceptibility.

The temperature-independent contribution to the susceptibility [φ in Eq. (4)] was found to be $15 \times 10^{-4} \text{ emu/mole}$ by Creveling and Luo.¹⁵ This is a difficult number to obtain accurately, and in fact Van Dam and Gubbens (and Kume) considered $\varphi = 0$. We wish to note, however, that a small value of φ calls for a large crystal-field splitting in the Kondo model. In particular, if we take Creveling and Luo's value, we find from Eq. (11) that $10D = 0.1 \text{ eV}$. This value is not unreasonable in view of the fact that the Korringa product for the nonmagnetic alloy AuNi suggests a crystal-field splitting which may be as large as 0.25 eV .¹⁰

From Eq. (11) we also find that $g = 1.8$. Although it is possible to relate the small difference $2 - g$ to the effects of spin-orbit splitting,¹⁶ such an analysis would be putting greater emphasis on the numerical aspects than is warranted at present.

Although for AuV the results predicted by the LSF model (when reasonable) are similar to those predicted by our results for the Kondo model,¹⁷ we expect greater differences between the predictions of the two models for other alloy systems. In particular, for the alloy system AlMn , which has been suggested by Schrieffer³ as possibly being a Kondo system with a very high T_K , a

similar analysis would tend to favor the LSF model over the Kondo model. In this case we suppose $n_d = 5$ (or 6) so that the spin Korringa product would be 7.8 (or 6.3). This would lead to a spin hyperfine field 1.6 (or 1.2) times as large as the already large hyperfine field predicted by the LSF model ($H_{\text{hf}}^d = -100 \text{ kOe}/\mu_B$).¹⁸

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¹P. W. Anderson, Phys. Rev. **124**, 41 (1961).

²J. Kondo, Progr. Theor. Phys. **32**, 37 (1964).

³J. R. Schrieffer, J. Appl. Phys. **38**, 1143 (1967).

⁴N. Rivier and M. J. Zuckermann, Phys. Rev. Lett. **21**, 904 (1968).

⁵H. Suhl, Phys. Rev. Lett. **19**, 442 (1967); M. J. Levine, T. V. Ramakrishnan, and R. A. Weiner, Phys. Rev. Lett. **20**, 1370 (1968).

⁶K. Kume, J. Phys. Soc. Jap. **23**, 1226 (1967).

⁷B. Caroli, P. Lederer, and D. Saint-James, Phys. Rev. Lett. **23**, 700 (1969).

⁸B. M. Boerstael and W. M. Star, Phys. Lett. **29A**, 97 (1969).

⁹J. E. Van Dam and P. C. Gubbens, Phys. Lett. **34A**, 185 (1971).

¹⁰L. Dworin and A. Narath, Phys. Rev. Lett. **25**, 1287 (1970).

¹¹A. Narath and A. Gossard, Phys. Rev. **183**, 391 (1969).

¹²L. Dworin, "Low Temperature Behavior of the Non-Degenerate Anderson Model of Localized Magnetic Moments," and "Low Temperature Behavior of the Multi-Orbital Anderson Model of Magnetic Impurities" (to be published).

¹³A. A. Migdal, Zh. Eksp. Teor. Fiz. **55**, 1964 (1968) [Sov. Phys. JETP **28**, 1036 (1969)].

¹⁴W. M. Star, thesis, University of Leiden, 1971 (to be published).

¹⁵L. Creveling, Jr., and H. L. Luo, Phys. Rev. **176**, 614 (1968).

¹⁶J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge U. Press, Cambridge, England, 1961), p. 349.

¹⁷Star (Ref. 14) has performed an analysis similar to ours using Nagaoka's results. However, in order to obtain agreement with the observed behavior, the value $S = \frac{1}{2}$ was required.

¹⁸A. Narath and H. T. Weaver, Phys. Rev. Lett. **23**, 233 (1969).

Studies on Nonmetals During Irradiation: The Growth of F Centers in KCl at 85°K*

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Curves of KCl F center versus dose, obtained by making absorption measurements during irradiation with Co^{60} γ rays at 85°K, are accurately described by $\alpha(t) = A_1[1 - \exp(-a_1 t)] + \alpha_L t$. After irradiation, the coloring decays less than 1% in 8×10^4 sec. A_1 is independent of, and a_1 and α_L are proportional to, the dose rate. These observations are in accord with a particularly simple phenomenological theory of radiation-induced color-center formation.

With very few exceptions, the radiation-induced formation of color centers in various crystals has been studied by the "traditional" technique of exposing the samples to an x-ray or γ -ray source and then transferring them to a spectrophotometer for measurement at a later time.^{1,2,3} Recently, both the KCl^{4,5} and NaCl⁶ F -center formation during irradiation and the growth and decay after irradiation have been studied at room temperature in facilities where absorption measurements can be made during Co^{60} irradiation. The earlier measurements were made at a maximum rate of 3×10^3 R/h; more recently, a maximum rate of 10^5 R/h has been made available.

This note describes the first measurements made at the higher dose rates on the formation of KCl F centers at 85°K. The results contain

several new features which are susceptible to an especially straightforward interpretation.

All measurements were made on samples cleaved from a single large crystal purchased from Harshaw Chemical Company. They were kept at 85°K in a Dewar cooled by liquid nitrogen but maintained at the desired temperature by an electronically controlled heater. The fused silica Dewar windows are shown by direct measurement to color negligibly. In addition, any absorption introduced is corrected by the double-beam spectrophotometer. This apparatus will be described elsewhere. Dose-rate measurements were made by thermoluminescent dosimetry techniques.

A selection of curves of F center versus dose recorded during irradiation at various dose rates