"ladders" and hence three series of oscillations. The measurements are being extended to higher magnetic fields in an attempt to observe further transitions which will enable an unambiguous identification to be made.

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INTRA-ATOMIC HUND'S RULE AND THE LOW-TEMPERATURE PROPERTIES OF NEARLY MAGNETIC DILUTE ALLOYS

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The localized spin fluctuation theory is shown to account for the observed values of the ratio $\xi = (\chi d\gamma/dc)(\gamma d\chi/dc)^{-1}$ in a number of dilute alloys of the AlMn type, when orbital degeneracy and intra-atomic Hund's rule coupling of the impurity are taken into account.

The theory of localized spin fluctuations[1] (hereafter called LSF theory) accounts fairly well for the properties of a number of dilute strongly paramagnetic transition metal alloys such as Pd:Ni,[2] Pt:Ni,[3] Rh:Co.[4] In the Friedel-Anderson model, the LSF theory,[5] which is qualitatively identical to the Wolff model, also predicts at low temperature a T^2 term in the resistivity and a temperature-independent susceptibility. Such a picture seems to describe correctly an alloy such as Al:Mn. However, the LSF theory, in both the Wolff-Clogston and Friedel-Anderson models, yields theoretical estimates for the ratio $\xi = (\chi d\gamma/dc)(\gamma d\chi/dc)^{-1}$ of the order of $\frac{3}{2}$, in serious disagreement with most experiments.[2,3,6,7] The value $\xi = \frac{3}{2}$ is obtained when a one-orbital model is used for the impurity, in the limit of strong local enhancement.[8]

In this Letter we shall discuss a more realistic model for alloys of the Al:Mn type taking into account the $(2l+1)$-fold degeneracy of the virtual bound state, and the existence of a Hund's coupling between the orbitals. Our main result is that (i) in the limit of zero Hund's coupling ($J_{mm'} = 0$) the theory yields $1 < \xi < \frac{3}{2}$ as in the one-orbital approximation while (ii) in the limit of strong Hund's coupling the

low-temperature renormalization of the specific-heat coefficient depends only on the "acoustic" fluctuating mode at the impurity, where the spin densities in all $5d$ orbitals fluctuate in phase together. There are $2l=4$ "optical" modes lying much higher in frequency which do not participate in the spin-fluctuation "dressing" of the localized d quasiparticles. Then the smallest theoretical estimate for ξ is $\frac{3}{2}(2l+1)$ in much better agreement with the experimental situation.

The Hamiltonian we use is a rotationally invariant modification of the Anderson Hamiltonian.[9] The interaction term of this model is

$$H_{\text{int}}=U\sum_{m,m'}n_{m\uparrow}n_{m'\downarrow}+\tfrac{1}{2}(U-J)\sum_{\substack{m\neq m'\\ \sigma}}n_{m\sigma}n_{m'\sigma}+J\sum_{m\neq m'}c_{m\uparrow}^{+}c_{m\downarrow}c_{m'\downarrow}^{+}c_{m'\uparrow}, \tag{1}$$

where $n_{m\sigma}=c_{m\sigma}^{+}c_{m\sigma}$ and $c_{m\sigma}^{+}$ ($c_{m\sigma}$) is the creation (destruction) operator for a d electron in the m orbital on the impurity cell.

Using the notation and the results of Ref. 9, the local susceptibility is

$$\chi(\omega)=\sum_{mm'}\chi_{mm'}(\omega).$$

With the random phase approximation,

$$\chi_{mm'}{}^{d}(\omega)=\left[\delta_{mm'}+\frac{J\chi_0(\omega)}{1-(U+4J)\chi_0(\omega)}\right]\frac{\chi_0(\omega)}{1-(U-J)\chi_0(\omega)}; \tag{2}$$

$\chi_0(\omega)=T\sum_{\omega_p}G_m(\omega+\omega_p)G_m(\omega_p)$ and $G_m(z)$ is the one-orbital Green's function in the Hartree-Fock approximation.[9] The LSF theory is based on the assumption that it is possible to have $(U+4J)\chi_0(0)<1$ and on the remark that

$$\chi_0(\omega)=\rho_d+i\pi\rho_d{}^{2}\omega+O(\omega^2), \tag{3}$$

where ρ_d is the density of states per impurity orbital at the Fermi level. Using (3) one can define a fluctuation temperature by

$$1-A\chi_0(\omega)=(1-A\rho_d)(1-i\omega/k_{\text{B}}T_f),$$

whence

$$k_{\text{B}}T_f=(1-A\rho_d)/\pi A\rho_d{}^{2}. \tag{4}$$

We have plotted, in Fig. 1, $\text{Im}\chi_{mm'}(\omega)$ as a function of frequency for the two limiting cases $J=0$ and $[1-(U+4J)\rho_d]^{-1}\gg[1-(U-J)\rho_d]^{-1}$. Two fluctuation temperatures T_{f_1} and T_{f_2} occur in the problem according to whether $A=(U-J)$ or $(U+4J)$ in (4).

From (2) we obtain, for a dilute alloy with a concentration c of impurities,

$$\Delta\chi=2\mu_{\text{B}}{}^{2}c(2l+1)\rho_d[1-(U+4J)\rho_d]^{-1}=\frac{2\mu_{\text{B}}{}^{2}c(2l+1)}{\pi k_{\text{B}}T_{f_2}}. \tag{5}$$

We also notice from (2) that the nuclear impurity Knight shift and relaxation time due to d electrons will be, respectively,

$$K_{\text{imp}}=\mu_{\text{B}}H_d\frac{(2l+1)\rho_d}{1-(U+4J)\rho_d}=\mu_{\text{B}}H_d\frac{2l+1}{\pi k_{\text{B}}T_{f_2}},$$

and

$$(T_1T)^{-1}=4\mu_{\text{B}}{}^{2}\gamma^{2}H_d{}^{2}\frac{k_{\text{B}}\pi\rho_d{}^{2}(2l+1)}{1-(U+4J)\rho_d{}^{2}}=4\mu_{\text{B}}{}^{2}\gamma^{2}H_d{}^{2}\frac{2l+1}{\pi k_{\text{B}}T_{f_2}},$$

so that the Korringa relation becomes

$$K_{\text{imp}}{}^{2}(T_1T)=(2l+1)(4\pi k_{\text{B}}\gamma^{2})^{-1} \tag{6}$$

independent of interactions and of potential scattering, as shown previously in the Wolff-Clogston model,[1] but depending on the orbital degeneracy through the factor $(2l+1)$. (H_d is the d hyperfine field and

γ the nuclear gyromagnetic ratio.) We obtain the specific heat from the free energy

$$\Delta F = \int_0^1 d\lambda (\partial F/\partial\lambda)(\lambda U, \lambda J).$$

The spin fluctuation contribution to ΔF is[10]

$$\frac{\partial F}{\partial\lambda} = \frac{3}{\pi}\int d\omega [n(\omega)+\tfrac{1}{2}]\,\mathrm{Im}\sum_{mm'} J_{mm'}\chi_{mm'}(\lambda U, \lambda J, \omega),$$

where

$$J_{mm'} = U\delta_{mm'} + J(1-\delta_{mm'});$$

then we obtain

$$\Delta F = \frac{3}{\pi}\frac{(2l+1)U}{U-J}\int_0^\infty [n(\omega)+\tfrac{1}{2}]d\omega\,\mathrm{Im}\,\ln\{1-(U-J)\chi_0(\omega)\}$$
$$+\frac{3}{\pi}(U+4J)\rho_d\int_0^\infty [n(\omega)+\tfrac{1}{2}]d\omega\,\mathrm{Im}\,\ln\frac{1-(U+4J)\chi_0(\omega)}{1-(U-J)\chi_0(\omega)}. \qquad (7)$$

From (7) we have, in the limit $J=0$,

$$\frac{\Delta\gamma}{c} = (2l+1)\pi\frac{k_B}{T_f}\left\{1-\frac{2\pi^2}{5}\left(\frac{T}{T_f}\right)^2\right\}+(2l+1)\frac{2\pi^2}{3}k_B{}^2\rho_d.$$

The last factor on the right is the usual Hartree-Fock potential scattering term. For $J=0$, $T_f = T_{f_1} = T_{f_2}$. Thus $\xi = 1-U\rho_d+\frac{3}{2}U\rho_d \simeq \frac{3}{2}$. In the limit $T_{f_1}/T_{f_2}\gg 1$, we have

$$\frac{\Delta\gamma}{c} = \pi(U+4J)\rho_d\frac{k_B}{T_{f_2}}\left[1-\frac{4\pi^2}{5}\left(\frac{T}{T_{f_2}}\right)^2\right]+(2l+1)\frac{2\pi^2}{3}k_B{}^2\rho_d.$$

Thus

$$\xi = 1-(U+4J)\rho_d+\frac{3}{2(2l+1)}[(U+4J)\rho_d]^2 = \frac{3}{2(2l+1)}. \qquad (8)$$

Experimentally it seems that Al:Mn alloys are a good example of LSF. The low-temperature properties are those of a normal Fermi gas. The susceptibility is temperature independent and the specific heat linear in T. The variation of the superconducting temperature versus impurity concentration is anomalous and is not explained solely in terms of pseudopotential corrections.[11] Low-resistivity measurements exhibit a temperature dependence of the form[5] $R = R_0[1-(T/T_f)^2]$ with $T_f \sim 530°$K. Mn Knight shift is very negative as expected from a strongly enhanced d-core polarization, T_1 is very short, and it is striking that the Korringa relation derived above [Eq. (6)] agrees with experimental data.[12] Furthermore in the alloy series Al:V, Al:Cr, Al:Mn residual resistivities increase slowly from V to Mn, while the susceptibilities and specific heat increase rapidly.[8] This is consistent with LSF picture,[5] where the residual resistivity is proportional to ρ_d while $\Delta\chi$ and $\Delta\gamma$ vary as described above.

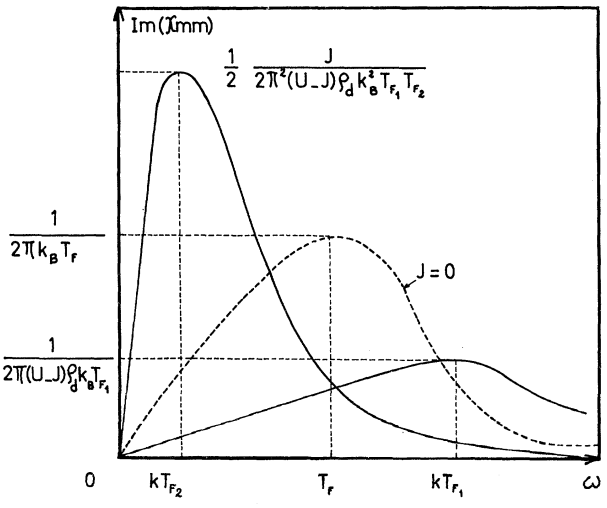

FIG. 1. The dashed curve is the form of $\mathrm{Im}\chi_{mm'}(\omega)$ obtained when $J=0$. Then $T_f = T_{f_1} = T_{f_2}$. The superposition of the two full curves yields $\mathrm{Im}\chi_{mm}$ when $J\neq 0$ and $T_{f_2} \ll T_{f_1}$.

In Table I we have listed the experimentally observed values for $\Delta\chi$ and $\Delta\gamma$ for a number of alloys. The ξ values obtained are in good agreement with our calculation [Eq. (8)] provided a strong Hund's coupling is present. We consider

Table I. Observed values of $\Delta\chi$ are given in the second column. The third column shows a rough estimate of $(\Delta\chi)_d$ corrected for a diamagnetic term estimated from Al:V data (Ref. 11). In the latter, the minimum paramagnetic contribution to $\Delta\chi$ is equal to $\Delta\gamma$ in eV^{-1}. Therefore the estimated diamagnetic correction for Al:Mn and Al:Cr is (in eV^{-1}) $\Delta\chi_{Al:V}{}^{obs}+\Delta\gamma_{Al:V}{}^{obs}$. The order of magnitude of the exact $\Delta\chi_{dia}$ should not change from Al:V to Al:Mn.

	$\Delta\chi_{obs}$ (eV^{-1})	$\Delta\chi_{corr}$ (eV^{-1})	$\Delta\gamma_{obs}$ (eV^{-1})	ξ_{obs}	ξ_{corr}	$T_f=\frac{2l+1}{\pi k_B \Delta\chi_{corr}}$ (°K)
Al:V[a]	−6.6	4.6±5	4.6±1.5			
Al:Cr[a]	11.2	22±4	6.7±1	0.6	0.8±0.1	750
Al:Mn[a]	22.5	33.5±1	9.5±1	0.41	0.28±0.06	500
Au:V[b-d]	58±25	?	21±?	0.36±0.2	?	250

[a]Ref. 8
[b]Ref. 11
[c]Ref. 12
[d]Ref. 13.

this as additional evidence for the validity of LSF theory in these materials. Notice also the satisfactory agreement obtained for Au:V alloys. Similar agreement seems to be obtained for other systems such as Au:Ti or Au:Co alloys.[13] Notice that the estimate for T_f in Au:V is similar to the estimate for T_{Kondo} in this system which has appeared in the experimental literature. This remark may support the conjecture[5] that T_f and what experimentalists call T_K should be closely related in some cases.

Although our theory is more adapted to alloys such as Al:Mn or Au:V which are well described in the Friedel-Anderson picture, it is obvious that our theory is qualitatively valid for such alloys as Pd:Ni, Ru:Fe, Ir:Fe, which are more suitably described in the Wolff-Clogston model. In some cases, as in Pd:Ni, one must also take into account the enhancement of the host, which is known to be much larger for the susceptibility than for the specific heat. For Pd:Ni, $\gamma^{-1}(d\gamma/dc)=17$, $\chi^{-1}(d\chi/dc)=87$, and $\xi=0.2$. The appropriate one-band model[1] yields $\xi=0.36$. It was argued by Engelsberg, Brinkman, and Doniach[14] that one could bring the theoretical estimate into agreement with the experiment by assuming a very large value for their range parameter σ around the impurity [$\sigma=13$ in Eq. (12), Ref. 14]. Although we have not treated in detail the orbital degeneracy for the Pd:Ni system, it seems to us more reasonable to resort to the simpler mechanism described here, since the nickel impurity, besides having $U_{Ni}>U_{Pd}$, has most certainly $J_{Ni}>J_{Pd}$. In the case of Pd:Ni, there are three bands of the T_{2g} symmetry at the Fermi level, therefore one can reduce the estimate for ξ of Ref. 14 by a factor as large as 3 for strong Hund's coupling. The fact that only a factor 2 is needed may indicate that Pd:Ni is in an intermediate situation as far as Hund's coupling is concerned.

Hund's coupling is also expected to have an important effect in such systems as Rh:Co and Ru:Fe; the reduction factor for ξ as compared with a one-orbital model will depend on the type of symmetry of the d bands at the Fermi surface in the host as well as the impurity cell.

As a matter of fact Doniach[15] has taken into account the effect of orbital degeneracy and Hund's coupling on the mass-enhancement effect in Pd. Our theory is quite similar to his. In the Pd problem, Schrieffer[16] argued that Hund's rule was not operative, because of the wave-vector dependence of the interaction. This argument does not hold in the local case. It is clear that even if $J\ll U$, one can have $[1-(U+4J)\rho d]^{-1}\gg[1(U-J)\rho d]^{-1}$.

We would like to conclude with the following remarks. In its present stage, LSF theory suffers from a major defect: It is based on the assumption that an exact treatment of the local interaction will yield values U_{eff}, J_{eff}, and $\chi_{eff}{}^0$ such that the condition $0<1-(U_{eff}+4J_{eff})\chi_{eff}{}^0<1$ can be fulfilled for certain values of U, ρ_d, E_F and that the low-frequency expansion of $\mathrm{Im}\chi_{eff}{}^0(\omega)$ is linear in frequency [Eq. (3)]. Recent work[17] indicates that the renormalized random phase approximation used by Suhl has this structure at low temperatures, at the cost of a redefinition of the parameter T_f. Furthermore, the discussion we gave in this Letter of the ξ values for a number of alloys has a meaning if the same enhancement coefficient $[1-(U+4J)\chi_0]^{-1}$ occurs in $\Delta\chi$ and $\Delta\gamma$. It is not clear that such will be the case in an exact treatment of the interaction. However the main result of our paper, namely that in the limit of strong coupling Hund's rule causes a decrease of ξ by a factor of $(2l+1)$, should hold in any theory. The rather satisfactory agreement between the simple theory described here and the experimental situation suggests that Hund's coupling has in-

deed a significant effect in alloys such as Al:Mn, Au:V, or Pd:Ni.

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EFFICIENT SENSITIZATION OF Ho^{3+} FLUORESCENCE*

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Conservation of the energy of green-light excitation was observed in the infrared fluorescence of a calcium-erbium fluoride crystal sensitized with TmF_3 and activated with HoF_3. Only the 2-μm transition of Ho^{3+} fluoresced at 77°K. Quantum yields up to 540% were observed in the fluorescence excitation spectrum. The linewidths, efficiency of fluorescence sensitization, and temperature dependence indicated ion-lattice interactions secondary to a resonant and nonresonant ion-ion interaction which was assigned to exchange.

Quantum yields greater than unity were predicted in Dexter's[1] theory of fluorescence sensitization through ion wave-function overlap interactions. The ion-pair transitions observed by Varsanyi and Dieke[2] supported resonance transfer in sensitization. Dexter[3] considered that the effect in a tight-binding approximation of electrostatic interaction was further conducive to efficient sensitization. Energy-conserving pair relaxation was reported by Porter and Moos.[4] Recently Ovsyankin and Feofilov[5] observed a concentration-dependent annihilation-creation process in sensitization which they distinguished[6] from Dexter's[1,3] concept of excitation quanta localized in summed ion levels. We had observed the effects seen by Ovsyankin and Feofilov in CaF_2-diluted erbium fluoride with TmF_3 and HoF_3 included as sensitizers and activators. A crystal tentatively identified as $Ca_2Er_5F_{19}$ then was prepared[7] in an attempt to obtain crystals of good optical quality at rare-earth (RE) concentrations higher than the 23 wt% solubility possible in CaF_2:(RE)F_3.

The 5145-Å sensitization was measured in a crystal of $Ca_2Ho_{0.05}Er_{4.90}Tm_{0.05}F_{19}$, 3×3 mm and 1.5 mm thick, mounted beneath a copper plug in a cylindrical quartz Dewar. The 5145-Å source was an argon laser of 40-μsec pulse length, 10 pulses per second, 0.33-W peak power, and 1.5-mm beam diameter at the crystal. A calibrated thermopile served as a radiometric standard. Fluorescence was detected with a 77°K, 25-mm^2 InSb cell, 25 mm from crystal center. The 2-μm fluorescence yield ϵ was obtained from the ratio (time integral of fluorescence power)/(average energy absorbed). Some anisotropy of the fluorescence radiance was observed and the radi-