

Anisotropy in metallic spin glasses arising from gold impurities

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Recent studies of *CuMn* alloys have shown that gold impurities introduce a large anisotropic coupling between the Mn ions. This coupling comes from the scattering of conduction electrons by the spin-orbit forces at the impurity sites. Since plane waves are scattered weakly by the spin-orbit interaction, the observation of strong anisotropy indicates that the orbital angular momentum of the conduction electrons in the vicinity of the gold impurity has been enhanced. The assumption that it is the *p* component which has been enhanced when the conduction electron wave function is orthogonalized to the *5p* core states of gold cannot explain the data. We have concluded that the *5d* shell of gold is not filled when gold is embedded in a copper matrix. A simple scaling argument shows that a vacancy of approximately $\frac{1}{6}$ of an electron in the *5d* shell accounts for the data. Our conclusion is supported by chemical valence data and provides an answer to an old mystery of the relative values of the residual resistivities of *CuAg*, *CuAu*, and *AgAu*.

Nonmagnetic impurities with significant spin-orbit interactions induce Dzyaloshinsky-Moriya (DM) interactions in magnetic alloys such as *CuMn* and enhance the macroscopic anisotropy of the spin-glass state. There exists a theory allowing one to calculate these interactions for transition-metal impurities.¹ However, gold is frequently used as the spin-orbit scatterer and it is not considered a transition-metal ion. Our aim is to calculate the DM interaction between magnetic ions induced by gold.

It is generally believed that the *5d* electrons of gold atoms interact weakly if at all with the conduction electrons of a metallic host. Thus, the experimental values of the spin-flip cross sections of gold impurities embedded in alkali metals have been attributed to the effects of the gold *5p* states.² Consequently, it is natural to assume that the *5p* states play a major role in creating the anisotropy of *CuMn* doped with gold, as observed by hysteresis loop,³ transverse susceptibility,⁴ and torque measurements.⁵ We find that the data cannot be explained by the effects of the *5p* core. We have concluded that the data can best be understood as arising from a vacancy in the gold *5d* shell of approximately $\frac{1}{6}$ an electron, i.e., that a partially vacant virtual bound state (VBS) develops at the gold site. Our conclusion is plausible in the light of chemical valence data and provides an answer to a long-standing question of the origin and relative values of the residual resistivities of the alloys *CuAu*, *CuAg*, and *AgAu*.

The effective interaction between two magnetic ions in metallic spin glasses is mediated by conduction electrons. Anisotropy arises when the electrons have been scattered by the spin-orbit forces of a third ion. Since plane waves are weakly scattered by the spin-orbit interaction, a mechanism is required which can augment the conduction electron's angular momentum components. One may assume that the

enhancement, rather than arising from *s-d* mixing as for Pt in *CuMn*, comes from the orthogonalization of the conduction electrons to the core states of the gold impurities, as in the traditional orthogonalized-plane-wave (OPW) model. Therefore, we calculate the effective third-order perturbation energy as in Ref. 1 but with an OPW-derived wave function instead of with the hybridized wave function corresponding to a virtual bound state.

In the OPW scheme, the wave function is given by

$$\psi_{k\sigma}^{\text{OPW}} = \left[e^{i\mathbf{k}\cdot\mathbf{r}} - 4\pi \sum_l i^l a_l(k) Y_{lm}^*(\hat{\mathbf{k}}) \psi_{sl,m}(\mathbf{r}) \right] \chi_{\sigma}, \quad (1)$$

where

$$a_l(k) = \int_0^{\infty} dr r^2 f_{sl}(r) j_l(kr).$$

In this expression, $f_{sl}(r)$ is the radial part of the core wave function $\psi_{sl,m}(r)$ and $j_l(kr)$ is the corresponding spherical Bessel function. Only the *5p* and *5d* states have been considered, as the *5s* states carry no orbital angular momentum and the overlap integrals $a_l(k)$ of the remaining states, e.g., *4f* are negligible.

The anisotropic coupling between Mn ions may be determined by calculating the change in energy of the electron gas due to the perturbation

$$V_{AB\lambda} = -\frac{\Gamma}{N} [\mathbf{S}_A \cdot \mathbf{s} \delta(\mathbf{r} - \mathbf{R}_A) + \mathbf{S}_B \cdot \mathbf{s} \delta(\mathbf{r} - \mathbf{R}_B)] + \lambda(r) \mathbf{l} \cdot \mathbf{s}, \quad (2)$$

where Γ is the effective exchange constant at the Mn sites, and $\lambda(r)$ is the spin-orbit coupling constant at the gold site. The third-order term of the Rayleigh-Schrödinger perturbation series, valid for continuum eigenfunctions, is given by¹

$$E^{(3)} = \left(\frac{1}{8\pi^3} \right)^3 \int_0^{k_F} dk_0 k_0^2 \int_0^{\infty} dk_1 k_1^2 \int_0^{\infty} dk_2 k_2^2 \left[\frac{P}{E_{k_0} - E_{k_1}} \frac{P}{E_{k_0} - E_{k_2}} - \frac{\pi^2}{3} \delta(E_{k_0} - E_{k_1}) \delta(E_{k_0} - E_{k_2}) \right] \\ \times \sum_{\sigma_0 \sigma_1 \sigma_2} \int d\Omega_{k_0} \int d\Omega_{k_1} \int d\Omega_{k_2} V_{k_0 \sigma_0, k_1 \sigma_1} V_{k_1 \sigma_1, k_2 \sigma_2} V_{k_2 \sigma_2, k_0 \sigma_0}. \quad (3)$$

The matrix elements $V_{k_i\sigma_i, k_j\sigma_j}$ are of the perturbation equation (2) taken between states of the conduction electrons given by Eq. (1). By using the spin interaction at sites A and B and the spin-orbit interaction at the ternary site in Eq. (3) we find that the leading (p and d) anisotropic coupling is given as

$$E_{AB\lambda}^{(3)} = - \sum_{l=2}^3 V_{OPW}^{(l)} \frac{P_{l-1}(\hat{\mathbf{R}}_A \cdot \hat{\mathbf{R}}_B) \cos[k_F(R_A + R_B + R_{AB})]}{R_A R_B R_{AB} (R_A + R_B + R_{AB})} (\hat{\mathbf{R}}_A \times \hat{\mathbf{R}}_B) \cdot (\mathbf{S}_A \times \mathbf{S}_B) ; \quad (4)$$

where

$$\left. \begin{aligned} V_{OPW}^{(2)} \\ V_{OPW}^{(3)} \end{aligned} \right\} = \frac{135\pi}{16} \frac{\Gamma^2}{E_F^2 k_F} \times \begin{cases} [-\frac{1}{3} \lambda_{5p} a_p^2(k_F)] \\ \lambda_{5d} a_d^2(k_F) \end{cases}$$

for orthogonality to the $5p$ and $5d$ core states, respectively. These coefficients take the place of V_1 in the DM interaction previously found by assuming a VBS at the ternary site.¹ In Eq. (4), P_{l-1} is a Legendre polynomial and λ_{5p} and λ_{5d} are defined by

$$\left. \begin{aligned} \lambda_{5p} \\ \lambda_{5d} \end{aligned} \right\} = \int_0^\infty dr r^2 \lambda(r) \times \begin{cases} |f_{5p}(r)|^2 \\ |f_{5d}(r)|^2 \end{cases}$$

The $(1/R^4)$ -type range dependence of the anisotropic coupling arises from the fact that electrons of all wave vectors are scattering rather than the scattering being dominated by wave vectors in a limited range around a resonance level located near the Fermi surface as in a VBS model.¹

For gold impurities in copper ($k_F = 1.36 \text{ \AA}^{-1}$), a simple numerical integration using the Herman-Skillman tables⁶ gives

$$a_p^2(k_F) = 0.037 \text{ \AA}^3, \quad a_d^2(k_F) = 0.032 \text{ \AA}^3.$$

However, for gold, $\lambda_{5p} \approx 20\lambda_{5d}$,² and since the macroscopic anisotropy is proportional to the sum of the squares of the DM interactions between the manganese ions, Eq. (4), it is easy to see that in an OPW model, the $5p$ contribution greatly exceeds the $5d$ contribution which is henceforth dropped.

From Eq. (4) we can represent the anisotropic pair interaction between a single Mn ion and all other Mn ions by¹

$$E_{DM}^{(i)} = \sum_{j>i} \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j. \quad (5)$$

Then the macroscopic anisotropy energy is given by^{4,5}

$$E_A = K(1 - \cos\theta), \quad (6)$$

where θ is the angle of rotation of the spin glass in an applied magnetic field. K is the anisotropy constant which is related to $E_{DM}^{(i)}$ by^{1,7}

$$K \sim \sum'_{ij} (D_{ij})^2. \quad (7)$$

To determine the efficacy of the gold $5p$ states in creating the observed anisotropy we compare the values of K found from the OPW and VBS models. For a VBS model, K has been estimated to be given by⁷

$$K_{VBS}^{(5d)} = \frac{64}{405} \left[\ln \frac{R_c}{R_0} + \frac{1}{2} \right] \frac{(V_1 S)^2}{V_0} yN, \quad (8)$$

where

$$V_1 = \frac{135\pi}{32} \frac{\lambda_{5d} \Gamma^2}{E_F^2 k_F^3} \sin\eta_2(k_F)$$

and the phase shift η_2 is given by

$$\eta_2(k_F) = \frac{\pi}{10} Z_d.$$

In this expression, R_0 is the nearest-neighbor distance in the host copper lattice and R_c is the interparticle distance where the DM interaction begins to take on a $1/R^4$ character.^{1,7} The parameter y is the ternary impurity concentration while V_0 is the Ruderman-Kittel-Kasuya-Yosida coupling constant and Z_d is the $5d$ charge at the nonmagnetic ternary site. An identical calculation using Eq. (4) yields

$$K_{OPW}^{(5p)} = \frac{4}{225} \frac{1}{R_0^2} \frac{(V_{OPW}^{(5p)} S)^2}{V_0} yN. \quad (9)$$

Thus, the ratio of the anisotropy constants for the materials CuMn_xAu_y and CuMn_xPt_y , the latter being described by a VBS model, is calculated to be

$$\frac{K_{OPW}^{(\text{Au})}}{K_{VBS}^{(\text{Pt})}} = \frac{9}{500} \frac{1}{R_0^2 [\ln(R_c/R_0) + \frac{1}{2}]} \times \left[\frac{\lambda_{5p}^{(\text{Au})} k_F^2 a_p^2(k_F)}{\lambda_{5d}^{(\text{Pt})} \sin\eta_2(k_F)} \right]^2. \quad (10)$$

For a copper host, $R_0 = a_0/\sqrt{2} = 2.55 \text{ \AA}$ and $R_c \approx 38.7 \text{ \AA}$.⁷ For gold impurities, $\lambda_{5p} = 12 \text{ eV}$. For platinum impurities, $\lambda_{5d} = 0.5 \text{ eV}$ and we assume that $Z_d = 9.4$ (Ref. 8) so that $\sin\eta_2(k_F) = 0.187$. Then the ratio [Eq. (10)] is

$$\left(\frac{K_{OPW}^{(\text{Au})}}{K_{VBS}^{(\text{Pt})}} \right)_{\text{theor}} = 0.06. \quad (11)$$

However, the experimental ratio is 0.18.⁹ It is clear that at best, the orthogonality of the conduction electron wave function to the $5p$ core states of gold can account for no more than one-third of the anisotropy observed in CuMnAu .

There is an additional argument against the importance of the core p states in creating anisotropy. Préjean *et al.*³ measured the field required to reverse the magnetization of CuMn doped with silver and found only a negligible increase ($< 60 \text{ Oe/at.}\%$) above the field required for CuMn . This result is in agreement with the effect calculated with the OPW approach and gives an indication of the minor role of the $4p$ states of Ag in CuMnAg : experimentally the ratio of $K^{(\text{Ag})}$ to $K^{(\text{Au})}$ is of order 1% while the ratio we calculate is of order 3%. From this comparison one sees that not only is the effect of the core p states negligible but that the OPW procedure overestimates the effect of the $4p$ states with respect to that of the $5p$ states by a factor of order 3. It is conceivable that the model also overestimates the contribution of the $5p$ states. Clearly another approach is required.

We note that copper and gold each have one valence electron but form compounds such as CuSO_4 and AuCl_3 in which their valences are 2^+ and 3^+ , respectively, as well as

compounds for which their charge states are 1^+ . Silver alone confines itself to valence 1^+ . These facts suggest that the d electrons of gold are not as tightly bound as one might suppose. Consequently if one postulates that the $5d$ levels of gold in a copper host are not too far below E_F , it follows that a partially vacant VBS may form on the gold sites. Then a simple scaling argument based on the VBS model [Eq. (8)] permits us to write

$$\left(\frac{K_{\text{VBS}}^{(\text{Au})}}{K_{\text{VBS}}^{(\text{Pt})}} \right)_{\text{theor}} = \left(\frac{K^{(\text{Au})}}{K^{(\text{Pt})}} \right)_{\text{expt}} = 0.18, \quad (12)$$

which is satisfied by taking $Z_d^{(\text{Au})} = 9.83$ for the number of localized d electrons for gold in copper if one accounts for the whole anisotropy by this mechanism. Even though the vacancy in the d shell is small (0.17 electron), its effect is sizeable. The hybridization of the conduction electron with the d states permits the electron to be scattered by the strong atomic spin-orbit force.

To corroborate our interpretation, we have considered the residual resistivities of the alloys CuAu , CuAg , and AgAu which are, respectively, 0.49, 0.07, and $0.38 \mu\Omega \text{ cm/at.}\%$.¹⁰ The standard expression for the residual resistivity is

$$\Delta\rho = \frac{4\pi N m v_F}{ne^2 k_F} \sum_l l \sin^2(\eta_{l-1} - \eta_l), \quad (13)$$

where N and n are the number of impurities and conduction electrons. If the $l=2$ term is presumed to dominate, then $\Delta\rho$ is proportional to $\sin^2\eta_2(k_F)$. By assuming that this equation is valid for a resonant scattering process, we can begin to understand the behavior of gold impurities. The residual resistivity of CuAu should be related to that of CuPt ($1.86 \mu\Omega \text{ cm/at.}\%$, see Ref. 11) by the equation

$$\Delta\rho^{(\text{Au})} = \frac{[\sin^2\eta_2(k_F)]^{(\text{Au})}}{[\sin^2\eta_2(k_F)]^{(\text{Pt})}} \Delta\rho^{(\text{Pt})}. \quad (14)$$

By setting $Z_d^{(\text{Pt})}$ equal to 9.4 and by using the experimental values of $\Delta\rho$, the solution is given by $Z_d^{(\text{Au})} = 9.70$. This value is consistent with that obtained by analysis of the anisotropy studies, i.e., 9.83. The low value of $\Delta\rho$ for CuAg with respect to that of both CuAu and AgAu may be understood within this picture by the fact that the $4d$ electrons of silver are tightly bound, as indicated by silver's simple chemical behavior discussed above. No VBS is formed. The low value of the anisotropy observed in CuMnAg is consistent with this argument.

Thus, by assuming that $Z_d^{(\text{Pt})}$ is unchanged from its accepted value when Pt is dissolved in Cu, it follows that a small vacancy of about $\frac{1}{6}$ an electron must develop in the

$5d$ shell of Au when Au is dissolved in Cu. If $Z_d^{(\text{Pt})}$ were in fact smaller, it would follow from Eq. (8) that $\sin\eta_2(k_F)$ would be larger so that by Eqs. (10) and (11) it can be seen that the discrepancy between the experimental and theoretical contributions of the $5p$ states to the anisotropy would widen. Then Eq. (12) would imply that the vacancy in the $5d$ shell of Au would be even larger.

There is an experimental way to determine the true effect of the $5p$ states on the anisotropy. It is well known that mercury forms valence-one and valence-two compounds such as $(\text{Hg})_2^+ \text{Cl}_2$ and $\text{Hg}^+ \text{Cl}_2$, but with two $6s$ valence electrons. Since trivalent mercury has never been seen in simple compounds, it is improbable that there is a partially occupied VBS when mercury is alloyed with copper. Since the overlap integrals $a_p(k_F)$ for Hg and Au in copper hosts are very nearly equal, experiments on CuMnHg should give the $5p$ contribution to the anisotropy energy by

$$K_{5p}^{(\text{Au})} = \left(\frac{\lambda_{5p}^{(\text{Au})}}{\lambda_{5p}^{(\text{Pt})}} \right)^2 (K^{(\text{Hg})})_{\text{expt}}. \quad (15)$$

On the basis of these considerations we predict that the anisotropy of CuMn doped with fifth-row impurities starting with platinum and continuing through polonium should show a minimum for mercury and thallium followed by a steady increase for lead, bismuth, and polonium. Although the spin-orbit forces in Hg and Tl are as strong as those in Pt and Au, these ions cannot scatter electrons via the s - d mixing interaction and therefore they will produce only a weak anisotropy. Beyond thallium, the increasing charge difference between these impurities and the host copper ions will lead to p wave screening. The resultant enhancement of the p component of the conduction electron wave function would then lead to an increasingly strong DM interaction. There is already some evidence for this. From studies of the ESR linewidth one finds that antimony produces strong anisotropic effects in AgMn .¹²

We conclude that the effect of gold $5p$ states is insufficient to explain the anisotropy produced by adding gold to CuMn . What has been observed is the effect of s - d mixing. In this sense gold impurities in copper act as transition-metal ions.

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