Oscillatory Exchange Coupling: RKKY or Quantum-Well Mechanism?

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The exchange coupling in multilayers of iron and chromium is calculated in the local spin density approximation, as a function of the Fe magnetic moment. We find a short-period and a long-period oscillation, which we attribute to a harmonic of the short period. For small moments, the interlayer coupling is found to be bilinear in the Fe moments, as assumed in RKKY theory. For moments appropriate to real iron the coupling tends to saturate, as assumed in quantum-well models, demonstrating that the quantum-well model more correctly describes the real iron-chromium system, though both models give correct periods of the oscillation.

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An exchange coupling between ferromagnetic layers, separated by a nonmagnetic metal layer, has been observed by a number of workers [1–4]. It was found, in fact, that this coupling oscillates as a function of the thickness of the intervening layer [5–8] with a period which is consistent with the Friedel-like oscillations [9] associated with the RKKY interaction [10]. For a multilayer geometry, this interaction takes the form $\sin(kx)/x^2$, with x the spacing between ferromagnetic (FM) layers and k a nesting vector at the Fermi surface. Remarkably enough, this same functional dependence is also consistent with a model in which quantum-well states are formed for a ferromagnetic alignment of the magnetic layers where, for example, all majority-spin bands lie below the Fermi energy and thus electrons of this spin at the Fermi energy are confined to the nonmagnetic layer [11]. Indeed, such quantum-well states have been observed in Fe/Ag by inverse photoemission [12]. In this case, the confinement arises from a gap in the minority-spin bands, as can be seen from the band structure of iron. The periods are the same because both depend directly upon the dimensions of the Fermi surface of the nonmagnetic material. This raises the question as to which of the models more appropriately describes the coupling. It cannot be decided on the basis of the periods alone since both predict the same periods. It is this question which we address here.

It must certainly be true that if the coupling between the magnetic moments in the magnetic materials and the conduction electrons in the combined system is weak enough, this coupling can be treated in second-order perturbation theory. This is exactly what is called RKKY coupling—it is oscillatory and bilinear in the magnetic moments on the two sides. If now the magnetization on each side becomes so strong that either the majority or the minority bands are shifted away from the Fermi energy E_F, quantum-well states will form near E_F. Confinement of these states gives rise to a term in the energy difference between the parallel alignment and antiparallel alignment, which is independent of the magnitude of the splitting of the bands and of the moment [13]. Thus, as the magnetic moments are smoothly increased from zero, the interlayer coupling will initially be proportional to the square of the moments, and second-order RKKY theory applies. Eventually quantum wells may form, and the interlayer coupling will saturate, becoming independent of the size of the moments. The system will shift smoothly between the two regimes, but we can distinguish which model is valid by noting the dependence upon moment. Although both models yield the same oscillatory behavior, the origin of the coupling in the two cases is fundamentally distinct. In RKKY, one spin polarizes the surrounding medium, while the other interacts with this polarization. In the quantum-well model, states are expelled from the Fe, and the confinement causes a discretization of states, which become more closely spaced with increasing spacer thickness. These give rise to an oscillatory dependence on the band structure energy as new states move below E_F. The effect resembles the de Haas–van Alphen effect in that only states at E_F enter [14]. The magnetic character of the magnetic layers plays no role in the quantum-well model except to provide two different shapes of quantum well, depending on the relative alignment of the magnetic layers.

Consider in particular the bands of nonmagnetic Cr and of FM Fe, all shown in Fig. 1. The minority-spin bands in Fe are similar to those in Cr, but shifted up slightly, with the Δ_2, $\Delta_{2'}$, and Δ_5 bands all crossing the Fermi energy . Thus for [001] multilayers, coupling is strong between minority-spin Fe and Cr bands. However, for the majority-spin bands of Fe, all three of those bands lie almost entirely below E_F. States of these symmetries are largely confined to the Cr, and quantum-well states formed when Fe slabs are ferromagnetically aligned.

Superlattices of [001] Fe/Cr offer an excellent test to distinguish the RKKY and quantum-well pictures. It was demonstrated previously [15] that, for nonmagnetic

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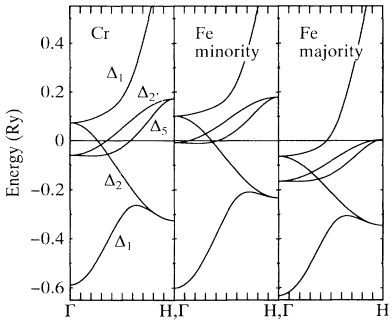

FIG. 1. Energy bands along [001] in Cr and Fe. First panel: bands of nonmagnetic Cr. Second and third panels: minority and majority bands of ferromagnetic Fe.

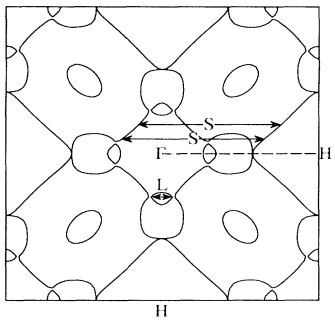

FIG. 2. Fermi surface of nonmagnetic Cr. Long vectors ("S") mark the large parallel sheets that give rise to 2.15 ML oscillatory coupling. The short vector ("L") has a length appropriate to the 12.3 ML period.

Cr, density-functional calculations yield oscillatory dependence of the exchange coupling E_x on the spacer thickness. The calculated variation of E_x with the number of Cr monolayers m was very well described by an RKKY form with two periods:

$$E_x(m) = \sum_{j=1}^{2} A_j \sin(q_j m + \phi_j)/m^2. \quad (1)$$

The periods $2\pi/q_j$ were determined by a least-squares fit to be 2.15 and 12.3 ML (monolayers), respectively, with the long-period amplitude about 5 times smaller than the short period. The short period is easily identified with the well-known nesting vector that gives rise to antiferromagnetism in Cr; these are marked "S" in Fig. 2. The long period is strikingly close to the value of 18 Å Parkin observed on [110] Fe/Cr [16], and also seen in the [001] whisker experiments [17] at high temperature. In this regard the calculated results are consistent with either the RKKY or quantum-well models. We can, however, distinguish the two models by observing the dependence of coupling strength on Fe moment.

To make such a study, we adopt a non-self-consistent procedure, which exploits the fact that self-consistent multilayer charge density deviates from bulk behavior only close to the interface. We approximate the self-consistent density by a suitably chosen trial density which is exact well away from the interface, and make use of the variational principle which states that errors in the total energy are second order in deviations from the self-consistent density. As discussed in Ref. [15], such trial densities, when combined with the Harris-Foulkes functional [18], are sufficient for a good description of the exchange coupling in Fe/Cr. As discussed in Ref. [15], we also add an additional step to the input potential across the interface, whose magnitude is determined variationally. This compensates for the missing dipole at the interface which must arise to align the bulk Fe and Cr Fermi levels.

A non-self-consistent approach is essential here, because a self-consistent calculation of necessity yields only a single density (and thus moment and coupling) for a given structure. We wish to obtain E_x as a continuous function of the Fe moment. Also in the special case of Fe/Cr, Cr manifests characteristics of an antiferromagnetic (AFM) spin-density wave; self-consistent solutions reflect this fact, as Ref. [15] discusses in detail. When Cr is antiferromagnetic, E_x does not exhibit the form Eq. (1) we seek here, but is dominated by the energetics intrinsic to the magnetic properties of antiferromagnetic bulk Cr, as modified by the presence of Fe at the boundary.

These calculations employ the atomic spheres approximation (ASA), which represents a crystal charge density by a superposition of overlapping, spherical, and atom-centered densities that fill space. The "combined correction" term, which accounts for a proper treatment of the muffin-tin potential in the interstitial region is included, and the usual basis of s, p, and d orbitals was employed. Integrations over the Brillouin zone are made with the linear tetrahedron method augmented with Blöchl weights [19], using a mesh of 48×48×4 divisions in the Brillouin zone. This was sufficient to converge E_x to about 2 μRy. A single average lattice constant of $a = 2.87$ Å was taken.

The trial density is constructed from the charge density of self-consistently calculated bulk nonmagnetic Cr in the Cr-centered spheres; in the Fe-centered spheres, a suitable average of bulk nonmagnetic Fe and ferromagnetic Fe was employed. Defining n^0 as the density of bulk nonmagnetic Fe, and n^+ and n^- as the spin densities of the majority and minority spins in ferromagnetic Fe, the density in the Fe spheres was taken to be

$$n_{\mathrm{Fe}}(r) = n^0(r) \pm \alpha \frac{n^+(r) - n^-(r)}{2}. \quad (2)$$

The Fe moment is proportional to α, reaching $2.28\mu_B$ corresponding to the density of bulk Fe at α=1. As stated earlier, the dependence of the A_j [Eq. (1)] on α enables us to distinguish the RKKY and quantum well limits.

As a preliminary test of this relation between coupling and moments we constructed a 54-atom chromium lat-

tice with two iron atoms substituted, each separated by 3 times the bcc nearest-neighbor distance, $3 \times \sqrt{3}a/2$. The 54-atom supercell consists of a $3a \times 3a$ cube with one iron at the origin and the other at $3a(111)/2$. The energy difference between inequivalent Fe atoms aligned parallel and antiparallel was then obtained as a function of the Fe moment, parametrized by α. In the context of RKKY theory, this energy difference is a superposition of the exchange interaction between all Fe pairs in the crystal, and varies as α^2. As Fig. 3 illustrates, the energy difference between ferromagnetic and antiferromagnetic alignment of the iron moments increases in proportion to α^2. The system is behaving just as would follow from RKKY theory, even up to the moment appropriate to real iron. (For $\alpha \approx 1$, there is a slight deviation, which is to be expected since RKKY coupling is obtained in second-order perturbation theory and valid only for small moments.)

We then constructed multilayer [001] superlattices of the type $Fe_2Cr_mFe_2Cr_m$, and calculated the energy difference $E_x = E[Fe_2^{\uparrow}Cr_mFe_2^{\downarrow}Cr_m] - E[Fe_2^{\uparrow}Cr_mFe_2^{\uparrow}Cr_m]$ as a function of α. For each α, the amplitudes A_j were determined by fitting E_x with the functional form Eq. (1). In this way, we determined the coupling strengths for both the short (A_1) and long (A_2) periods independently as a function of Fe moment, as Fig. 3 illustrates. For small α, the couplings of both short and long periods increase as α^2, as expected. At larger α both couplings show evidence of saturating, with the long period saturating completely. The deviation from the α^2 line definitely indicates a breakdown of the RKKY theory near the observed iron moment. To the extent that the couplings saturate, one can say that the quantum-well theory applies. However, the tendency of the short-period amplitude to continue its rise at large α indicates that the behavior is not as simple as the quantum-well picture with complete confinement would suggest.

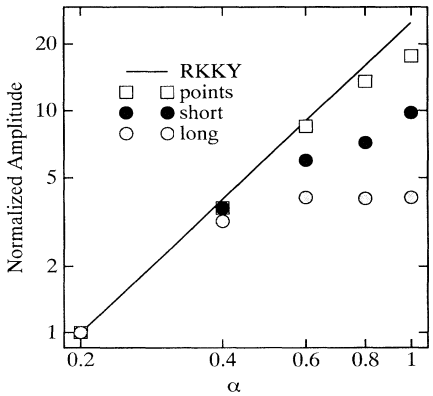

FIG. 3. Exchange coupling as a function of normalized Fe moment α. α=1 corresponds to bulk Fe, or $2.28\mu_B$. All couplings are scaled to unity at α=0.2. Straight line, α^2; squares, E_x of the 54-atom supercell; dark circles, short-period amplitude; light circles, long-period amplitude.

A closer look at the band structure of chromium indicates why this might be so. Let us consider the short period first. We showed earlier that quantum wells can arise when the spacer encounters gaps at the boundary, and that such gaps are present along the Γ-H line (Fig. 1) because states of different symmetry do not couple. All the bands shown in Fig. 1 have wave vectors exactly normal to the interface. But it is evident from Fig. 2 that the vectors responsible for the short period span a large portion of the Brillouin zone. Electrons with transverse components to their wave numbers have mixed symmetry and are no longer decoupled. Confinement is complete only for normal wave vectors (and possibly wave vectors at other high-symmetry points); elsewhere the quantum well becomes "permeable." Thus, the quantum-well model is only approximate, states being confined to a greater or lesser degree throughout the Brillouin zone. It would be erroneous, however, to attribute the quantum-well part of the coupling to states with small transverse wave vector and the RKKY coupling elsewhere. As the "S" nesting vector in Fig. 2 approaches the Γ-H line, corresponding to normal incidence, we may see by comparison with the bands of Fig. 2 that one end approaches $\Delta_{2'}$ symmetry and the other Δ_5 symmetry. They cannot belong to the same quantum-well states at that point and thus do not contribute to the observed oscillatory period. For the same reason, they do not contribute to an RKKY coupling. The coupling arises from the large, approximately planar, Fermi surfaces of the electron surface centered at Γ and the hole surface centered at H, a projection of which is shown in Fig. 2.

What is the origin of the long period coupling? The only nesting vector that seems to approximately match the 12.3 ML period is that marked "L" in Fig. 2 [20]. This vector is unlikely to be responsible for the 12.3 ML period for several reasons. The phase space associated with that nesting vector is small; moreover, it connects states of different symmetry. This reduces coupling strength and in the RKKY description the envelope function falls off faster than the usual $1/m^2$. To check this possibility, we attempted to fit the calculated coupling using a $1/m^4$ envelope for the long period. The fit was significantly worse than with a fit with a $1/m^2$ envelope, and was essentially no better than a fit using a single, short period. There do not seem to be any other nesting vectors of the appropriate length, particularly ones that connect states of the same symmetry.

The 12.3 ML period would, however, seem to match quite well a "Vernier" period of the *first harmonic* of the short-period oscillation. A free-electron description of the quantum-well limit shows that the oscillatory coupling is not strictly harmonic, but has a sawtoothed shape [21]. Our own unpublished tight-binding calculation agrees with this. To the extent that a quantum-well description is valid, higher harmonics should be present which add terms of the form $m^{-2}\sin(2\pi nm/T + \text{phase})$, with T the fundamental period and $n = 2, 3, \ldots$. Ex-

pressing the 2.15 ML period T_1 as $1/T_1 = 1/2+\delta/2\pi$, the lowest (n=2) harmonic becomes $m^{-2}\sin(2\delta m + \text{phase})$. This "Vernier" period has *exactly the same form* as Eq. (1), with an effective period $T_2 = 2\pi/2\delta = T_1/(2 - T_1)$. (A "Vernier" period—sometimes called "aliasing"—describes beats that arise when a simple harmonic function is sampled on a slightly incommensurate mesh. That is the origin of this term, except here it arises from the $n = 2$ harmonic of the short period.) Using the calculated value of 2.15 ML for the short period, we obtain an effective interaction with a period $T_2 = 2.15/0.15 = 14.3$ ML. This value is slightly larger than the fit value of 12.3 ML, which would correspond by a short-period nesting vector of 2.177 ML, or about 1% larger than 2.15 ML. The discrepancy cannot be attributed entirely to uncertainties in the fit by Eq. (1), as the uncertainty is $\approx$0.01 ML for the short period and $\approx$0.5 ML for the long. However, the 2.15 ML period is actually some weighted average of the "S" vectors in Fig. 2, which fluctuate by about 3% because the planes bow slightly [20]. The higher harmonic arises from a different weighted average, so that the effective "average" vector corresponding to the Vernier period may differ by something less than 3%.

Why does the long period completely saturate? We noted that higher harmonics are present in the quantum-well limit. Corresponding higher-order terms do not occur in the same form in RKKY theory; in that case all of the higher-order terms depend in the same way on the coupling strength, and take the form $\sin(2\pi m/T + \text{phase})/m^{2+\text{integer}}$. That is, the corrections to Eq. (1) alter the *envelope* rather than the *oscillatory* part [21]. A Vernier period is thus a *signature* of the quantum-well description. The long period saturates completely because it originates from the quantum-well character of the 2.15 ML interaction; the RKKY character does not contribute.

To summarize, we see in a consistent way how the short period in FeCr makes a partial transition to a quantum-well character from an RKKY description at small moments. The transition is partial because of the incomplete confinement of states in Cr, and manifests itself as an incomplete saturation of the interaction with Fe moment. The origin of the long-period interaction also emerges naturally from this picture, as a manifestation of higher harmonics stemming from the quantum-well character of the interaction. The first harmonic appears as an *effective* interaction with a period of approximately 12 ML, matching well with the period actually observed. Its saturation with Fe moment offers further evidence of a quantum-well description of the exchange coupling.

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