Heat-induced antiferromagnetic coupling in multilayers with ZnSe spacers

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(Received 16 Feburary 1999)

Two ferromagnetic films separated by an amorphous semiconducting spacer are exchange coupled across the spacer layer. The coupling is reversibly temperature dependent with a positive temperature coefficient. As spacer material we use amorphous ZnSe which is a compound semiconductor and find heat-induced antiferromagnetic coupling in striking similarity to amorphous Si and Ge. In an Fe/*a*-ZnSe/Fe trilayer with spacer thickness between 18 Å and 22 Å the coupling is antiferromagnetic with a positive temperature coefficient. At slightly larger thicknesses between 22 Å and 25 Å we find a reversible transition from ferromagnetic coupling at low temperatures to antiferromagnetic coupling at higher temperatures upon heating. We discuss the reversibly heat-induced effective exchange coupling in terms of localized defect states in the band gap in the vicinity of the Fermi energy. [S0163-1829(99)04230-7]

In multilayers consisting of ferromagnetic and nonmagnetic ultrathin layers the quasi-two-dimensional symmetry is responsible for outstanding effects. The extremely long range of the oscillatory exchange coupling between ferromagnets across metallic spacers[1,2] is a consequence of this symmetry. Another consequence is that it makes an effective exchange coupling possible with a positive temperature coefficient if amorphous semiconductors are involved as spacer materials. Iron layers that are separated by an amorphous Si or Ge spacer are indeed exchange coupled, and the coupling strength reversibly increases upon heating. An important quality common to the systems which exhibit a reversibly positive temperature coefficient or ''heat-induced coupling''[3–5] is that they are amorphous and prepared at very low temperatures. In striking contrast, multilayers of Fe and Si or Ge that are prepared at room temperature exhibit coupling which is stronger by two orders of magnitude and have a conventional temperature dependence.[6–13] The reason for this difference is that the spacers of multilayers prepared at higher temperature are crystalline metallic Fe-Si compounds[12] and not amorphous semiconductors. Recent investigations of crystalline ZnSe as a spacer material between Fe layers also show only ferromagnetic coupling with an almost temperature independent coupling strength.[14]

Although it is believed that the symmetry of the quasi-two-dimensional layers is essential for this heat-induced effective coupling to occur, a quantum mechanical description of it does not yet exist. In this study we set out to gain further insight, and eventually provide a base for a theoretical ansatz. We demonstrate the occurrence of the effect on a new and different system: ferromagnetic layers with amorphous ZnSe spacers on crystalline substrates. Using *in situ* magnetometry with spin-polarized secondary-electron emission we find, as a main result, antiferromagnetic coupling across amorphous ZnSe to occur. In addition, we provide a quantitative determination of the coupling strength as a function of spacer thickness and temperature by measurements with the conventional magneto-optical Kerr effect. Further, we observe that the last step of the sample preparation must be carried out at temperatures below 150 K for the antiferromagnetic coupling to occur, and that mild annealing at 250 K irreversibly destroys it. We interpret this fact as an apparent necessity for defect states to be present, maybe at the interface, in order to mediate the coupling.

Sample preparation and magnetic measurements are performed in an UHV chamber with a base pressure of 5×10^{-11} mbar. A sputter cleaned and annealed Cu(100) crystal is the substrate. We first evaporate at 90°C a 70 Å thick Co film which serves as a magnetic driver. A 6 Å Fe layer, which is strongly coupled to the Co film, makes sure that the interface conditions are comparable to the previous experiments with Si and Ge spacers. Then the sample is cooled down to 20 K for the preparation of the ZnSe spacer, which is evaporated from powder in a W crucible.[15,16] The sample is completed by a 15 Å thick Fe layer. The cleanliness of the sample is checked by standard Auger electron spectroscopy (AES). Within the resolving power of AES we do not find any interdiffusion to occur. We note that evaporation at low temperatures is strictly necessary only for the Fe top layer. Prior to the measurements of the coupling strength the sample must be briefly annealed at 150 K presumably to form the appropriate interfaces.

We use surface magnetometry by spin polarized secondary electron emission (SPSEE) to determine the thickness dependence of the effective exchange coupling and to address the importance of a possible 90° component. A 1-5 keV primary electron beam produces a cascade of secondary electrons on the sample surface. A subsequent spin analysis of the emitted secondary electrons with reference to the two in-plane quantization axes is carried out in a 100 keV Mott detector. The spin polarization P, defined as $P=(N\uparrow-N\downarrow)/(N\uparrow+N\downarrow)$, is proportional to the magnetization of the sample at the surface.[17,18] $N\uparrow$ and $N\downarrow$ are the number of electrons with spin parallel and antiparallel to the chosen quantization axis, respectively. The high surface sensitivity allows us to directly probe the magnetization of the outermost layer. In our coupling experiments, we monitor the response of an exchange coupled surface layer with respect to the magnetization of a bottom layer on the magnetic driver and in this way study the exchange coupling across a particular spacer material between surface layer and bottom layer. In order to determine coupling strength as a function

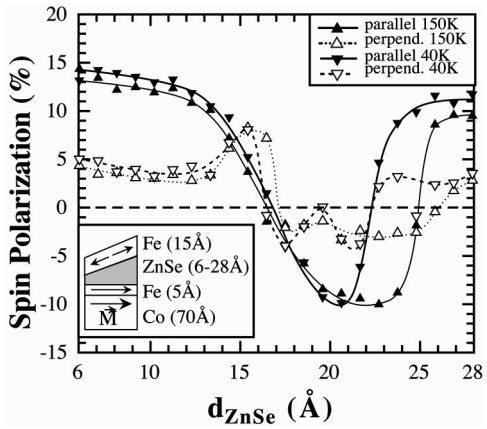

FIG. 1. Spin polarization P of secondary electrons at remanence of the top Fe layer of an Fe/a-ZnSe(wedge)/Fe sample deposited on a 70 Å Co/Cu(100) substrate, vs ZnSe spacer thickness. In-plane components parallel and perpendicular to the magnetizing field are shown. The change between the behavior at 40 K and at 150 K is fully reversible.

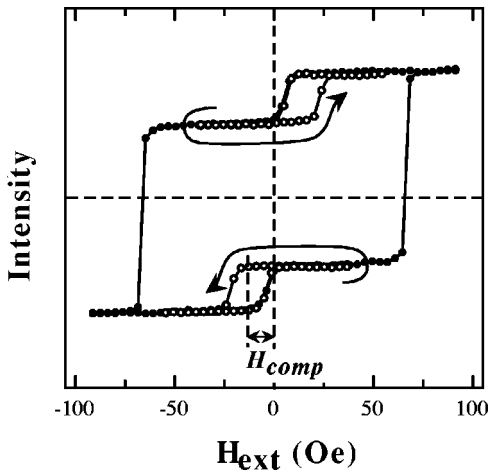

FIG. 2. MOKE signal of a 15 Å Fe/25 Å ZnSe/6 Å Fe/70 Å Co/Cu(100). Two minor loops originating from the top layer only are shown by open circles; the dots represent a complete hysteresis loop.

of temperature we use *in situ* magnetometry by the magneto-optical Kerr effect (MOKE). As opposed to the SPSEE measurements, MOKE is less surface sensitive and therefore a signal originating from top layer, bottom layer, and magnetic driver is detected. In the present study we use the longitudinal geometry.

First we address the thickness dependence of the exchange coupling across amorphous ZnSe. To do so we prepare a sample with a wedge-shaped spacer layer. Then we magnetize the Co magnetic driver by an external magnet field pulse and perform SPSEE measurements of the polarization P at remanence along the wedge. The signal P originates from the top layer only. It therefore reflects the direction of the top layer magnetization with respect to the one of the magnetic driver. As a result the dependence of the two in-plane components of P at remanence on the spacer thickness is shown in Fig. 1. Data measured on the same sample at 40 K and at 150 K are presented. The P signal yields that for different spacer thicknesses different types of exchange coupling do occur. Below 14 Å we find that the top layer magnetization is parallel to the magnetic driver magnetization and saturated, which stands for strong ferromagnetic coupling. Then, between 14 Å and 17 Å, a strong perpendicular component indicates that in this intermediate range 90° coupling prevails. In a spacer thickness range between 18 Å and 22 Å the top layer magnetization points in the negative direction with respect to the magnetic driver magnetization and the external field pulse direction. This unambiguously demonstrates the occurrence of antiferromagnetic coupling. Most striking, between 23 Å and 25 Å, the coupling is antiferromagnetic at 150 K, whereas at 40 K we find a magnetization pointing in the positive direction. This corresponds to a reversible transition from ferromagnetic to antiferromagentic exchange coupling upon heating. Above 25 Å the Fe top layer magnetization is parallel to the driver magnetization indicating either ferromagnetic or very weak coupling with a coupling strength that is not sufficient to overcome the top layer coercivity.

The positive temperature coefficient of the coupling strength certainly is the most outstanding aspect of exchange coupling in multilayers with semiconducting spacers. The observed broadening of the antiferromagnetic region with increasing temperature shown in Fig. 1 indeed points to an exciting temperature dependence. In the following, we investigate the temperature dependence of the coupling strength by measurements of the compensation field H_{comp} using MOKE. H_{comp} is the external field necessary to cancel out the ferromagnetic or antiferromagnetic interlayer exchange coupling. It is strictly proportional to the coupling strength. An example of a MOKE measurement on an antiferromagnetically coupled Fe/ZnSe/Fe/Co/Cu(100) sample is shown in Fig. 2. Since for most of the samples the coercivity of Co/Cu(100) magnetic driver is higher than the ferromagnetic or antiferromagnetic coupling strength, we use the following procedure for determination of H_{comp}: We apply a magnetic field pulse in one direction in order to define the magnetization of the Fe/Co bottom layer. Then a hysteresis loop of the top layer is measured, during which the applied field does not exceed the coercivity of the bottom layer. A *minor loop* results, as depicted by the circles in Fig. 2. Next the bottom layer magnetization is reversed and again a top layer hysteresis loop is measured. The shift between the centers—the remanent states—of the two loops along the external field axis then reveals the compensation field $2H_{comp}$ and hence the strength of the antiferromagnetic or ferromagnetic coupling. The major steps in the MOKE signal in Fig. 2 (dots) stem from the reversal of the Fe/Co substrate magnetization. With this scheme we identify heat-induced antiferromagnetic interaction and a sign change from ferromagnetic to antiferromagnetic coupling upon heating, depending on the spacer thickness. We strongly emphasize that the temperature dependences to be discussed below and hence the term ''heat-induced'' always refer to *reversible* effects.

As an example, Fig. 3 depicts MOKE minor hysteresis loops at different temperatures of an Fe/$a-$ZnSe/Fe trilayer with a ZnSe thickness of 30 Å. As we can see in the figure, at $T=30$ K the particular minor loop (dots) corresponding to the substrate magnetization in the positive or right side direction appears on the *left* side of the other one (circles). This stems from a weak ferromagnetic coupling. Upon heating, a

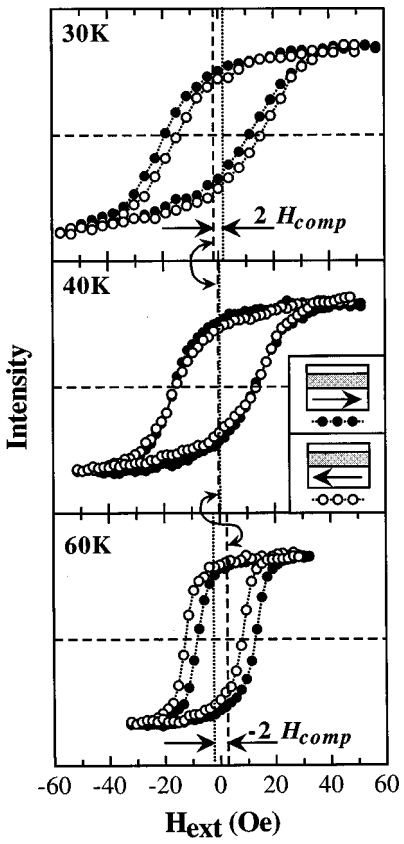

FIG. 3. MOKE minor loops originating from the top Fe layer of an Fe/30 Å a-ZnSe/Fe structure. Dots and open circles represent measurements with the Co magnetic driver magnetization parallel and antiparallel to the positive field direction, respectively. The displacement of the loops along the field axis corresponds to the compensation field H_{comp}. The sign change of the compensation field upon heating from 30 K to 60 K is fully reversible.

reversible shift of the two loops along the axis of the external field occurs. They eventually cross at around 40 K. With this a reversible transition from very weak ferromagnetic coupling to weak antiferromagnetic coupling is established.

Measurements of the coupling strength J as a function of temperature for different samples with a variety of spacer thicknesses are compiled in Fig. 4. We find that the data exhibit a considerable thickness dependence concerning the absolute coupling strength whereas, however, the temperature dependence looks remarkably uniform for all antiferromagnetically coupled samples. In all cases, the positive temperature coefficient is most evident at low temperatures, and the coupling strength reaches saturation at $T \approx 100$ K. We note that the thickness dependence of the coupling strength at 40 K is not completely consistent with the measurement shown in Fig. 1. We attribute this to the fact that the data presented in Fig. 4 have been recorded later in the course of the experiments. A slight shift to higher spacer thicknesses for which the coupling occurs is observed if the ZnSe evaporators have been used for a long time.

The determination of the effective coupling strength from a compensation field is straightforward. In an external magnetic field the top layer magnetostatic energy HVM_S competes the coupling energy JA, if the magnetization of the Fe/Co bottom layer is fixed. M_S,V, and A are saturation

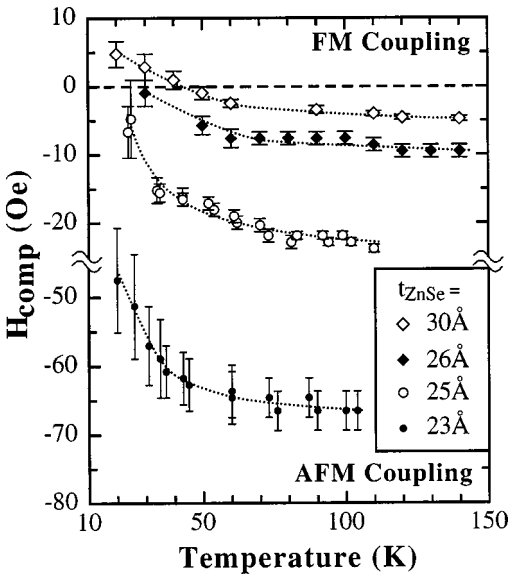

FIG. 4. Compensation field $H_{comp} \propto -J$ vs temperature for a variety of spacer thicknesses. In the temperature range chosen, all temperature dependences are fully reversible. We observe that the coupling of samples with larger spacer thicknesses undergoes a sign change.

magnetization, volume, and area of the Fe top layer, respectively. H_{comp} by definition is the field at which the two energies are equal. Thus,

$$J = t_{Fe} M_S H_{comp}. \tag{1}$$

For a compensation field of $H_{comp} = 20$ Oe, in the antiferromagnetic regime, we estimate $J = 8 \times 10^{-6}\,\mathrm{J\,m^{-2}}$.

Next, we address the irreversible part of the temperature dependence of J. In Fig. 5 the effect of heating an antiferromagnetically coupled sample to higher temperatures than 200 K is presented. We find that upon heating beyond 200 K the antiferromagnetic coupling strength reduces and the coupling becomes ferromagnetic. This transition is irreversible. After the transition the coupling is always ferromagnetic and almost independent of temperature, as shown in Fig. 5.

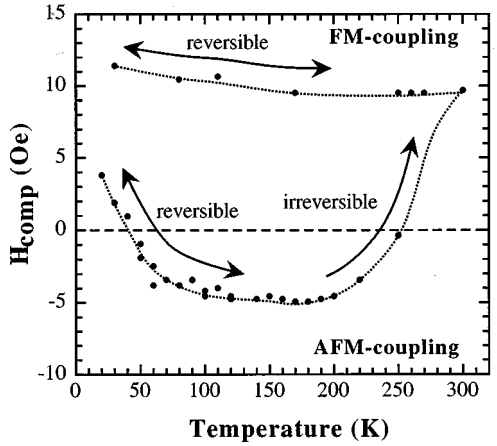

FIG. 5. Compensation field $H_{comp} \propto -J$ vs temperature of a multilayer with spacer thickness $t_{ZnSe} = 30$ Å. Upon heating to above 200 K we observe an irreversible transition to ferromagnetic coupling with a weak temperature dependence.

For the remainder of the paper we discuss the intriguing temperature dependence of the exchange coupling. As in our earlier studies on *a*-Si (Refs. 3 and 4) and *a*-Ge (Ref. 5) we adopt the picture of defect states as being responsible for the coupling to occur. An understanding of the irreversible transition upon annealing at temperatures well below room temperature provides key information on the nature of the effective coupling. Comparison with exchange coupling experiments carried out on epitaxial Fe/ZnSe/Fe,[14] which has to be prepared at temperatures as high as 200°C, makes us confident that the irreversible transition at 200 K is not due to a chemical or interdiffusion process. On the contrary, the Fe/ZnSe interfaces are stable up to temperatures far above room temperature.[14,19] Also crystallization of the *a*-ZnSe can be ruled out as the driving force behind the transition since $T_{cryst} \approx 170°C$ is far above room temperature. From this we infer that defect states in the spacer material or at the interface mediate the heat-induced effective exchange coupling.

Whereas point defects in crystalline semiconductors are likely to produce shallow donors or acceptors which dominate the electronic properties of the semiconductor already at comparatively low concentrations, the situation is completely different for amorphous semiconductors. There, the semiconductor gap is replaced by the mobility gap. Within this mobility gap, the density of states (DOS) is reduced compared to valence and conduction band DOS and the states are localized. While the random potential resulting from the amorphous structure produces tails of localized states close to conduction or valence bands, the existence of point defects such as dangling bonds or impurities leads to an increased density of localized states around E_F. However, as opposed to crystalline semiconductors, defects also in higher concentrations do not provoke metallic properties via the existence of impurity bands. It is known[20] that at low temperatures defect states close to E_F are responsible for the electronic transport in amorphous semiconductors through a hopping mechanism. Consequently, as a starting point it is reasonable to assume that these defect states also provoke an effective exchange coupling between two ferromagnetic layers across an amorphous semiconductor.

Next we give a rough argument why defect states around E_F can cause a positive temperature coefficient and saturation at low temperatures of the coupling strength. We follow a line of thought given by Briner.[21] First we assume that each defect state in the spacer mediates a certain contribution to the effective exchange energy which is the same for all defects and does not depend on temperature. Such a coupling process, like resonant tunneling, requires there to be empty and occupied states in the ferromagnetic layers, respectively. However, both of them are available only in an energy window $\sim k_B T$ around E_F. If we further assume the defect states to have constant DOS, the coupling strength then is proportional to $\int F(E)((1-F(E))dE$, $F(E)$ being the Fermi-Dirac function. Now, as theoretical models suggest[20] and experiments confirm,[22] the defect states in the spacer are peaked around E_F. On the simplifying assumption that the peak has a square form with width $2\Delta E$, we then get[21]

$$J \propto \int_{-\Delta E}^{\Delta E} F(E)(1-F(E))dE = k_B T \frac{\sinh(\Delta E/kT)}{1+\cosh(\Delta E/kT)}. \tag{2}$$

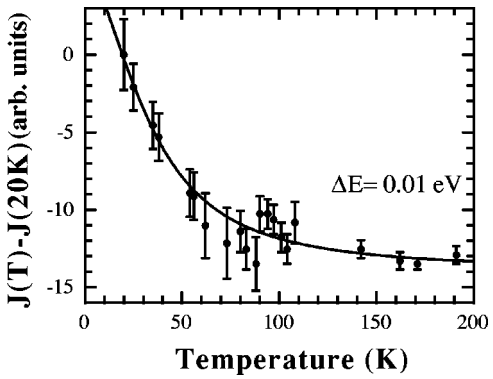

FIG. 6. Antiferromagnetic coupling strength vs T according to Eq. (2) (solid line), compared to a typical measurement (squares).

Equation (2) reproduces the positive temperature coefficient of the coupling and also describes how saturation can be reached well below the Curie temperature of the ferromagnets. The fact that the coupling strength is saturated at temperatures around $T_{sat} = 100$ K sets an energy scale for the possible excitations of $\Delta E \sim k_B T_{sat} = 0.01$ eV. In Fig. 6 we show that Eq. (2) can indeed describe the measured behavior. However, Eq. (2) is based on very simplifying assumptions. The agreement to the measured data should be taken to be only a qualitative finding. The defect distribution width $2\Delta E$ as obtained from the displayed fit, for example, is one order of magnitude short of what has been reported from room temperature transport measurements.[22]

Coupling measurements carried out on *epitaxial* Fe/ZnSe/Fe have revealed only ferromagnetic coupling with an almost temperature independent coupling strength.[14] The differences between those observations and the present findings arise from specific preparation conditions which lead to entirely different spacer materials. We infer that defect states are decisive for the heat-induced exchange coupling to occur. Therefore it is straightforward that in a crystalline spacer such a coupling should not be present, well in line with observation.[14] The question whether the small ferromagnetic offset in our data that produces the sign change as a function of temperature for larger spacer thicknesses, on one hand, the ferromagnetic coupling that persists after annealing to above 200 K, on the other, and the ferromagntic coupling across crystalline ZnSe spacers,[14] third, are all of the same origin, remains open for further investigations.

In summary, we present evidence for heat-induced antiferromagnetic exchange interaction in a new system: Fe/*a*-ZnSe/Fe trilayers. We find that completion of the sample below 150 K is essential and that annealing above 200 K removes the antiferromagnetic coupling. We infer that localized defect states in the gap are responsible for the coupling and its positive temperature coefficient and present a simple model based on a uniform contribution to the effective exchange energy and a constant DOS of the defects.

It is a pleasure to thank H.C. Siegmann for continuous support and fruitful discussions and K. Brunner for expert technical assistance. We also would like to express our gratitude to S. Lüscher for carrying out essential precursory experiments. Financial support by the Schweizerischer Nationalfonds is gratefully acknowledged.

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