

Finite Tunneling Spin Polarization at the Compensation Point of Rare-Earth-Metal–Transition-Metal Alloys

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We show, using superconducting tunneling spectroscopy and tunneling magnetoresistance measurements, that ferrimagnetic alloys of Co and Gd can exhibit both positive and negative spin polarization depending on temperature and composition. These observations can be understood by considering the relative contributions of independent spin-polarized tunneling currents from the rare-earth-metal and transition-metal subnetwork magnetizations, which are coupled antiferromagnetically. At the compensation point of the alloy, where the subnetwork magnetizations are equal and the alloy has nearly zero net magnetization, nevertheless large tunneling spin polarization is observed.

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Magnetic tunnel junctions (MTJs) are composed of sandwiches of two ferromagnetic (F) layers separated by thin insulating (I) layers [1–4] that display large tunneling magnetoresistance (TMR) at room temperature of up to 70% using Al₂O₃ tunnel barriers [5] and more than 220% using MgO tunnel barriers [6]. MTJs are attractive for field sensing and magnetic memory applications. The resistance of the MTJ depends on the relative orientation of the magnetizations of the F electrodes. Here we define $TMR = (R_{AP} - R_P)/R_L$ where R_{AP} and R_P correspond to the resistance for antiparallel and parallel alignment of the F electrodes' magnetizations, respectively, and R_L is the lower of either R_P or R_{AP} . The TMR originates from the spin polarization of the tunneling current that can be measured most directly using superconducting tunneling spectroscopy (STS) in related tunnel junctions in which one of the ferromagnetic electrodes of the MTJ is replaced by a thin superconducting (S) layer. The TMR and spin polarization are then simply related according to Julliere's model [1].

The origin of the sign and magnitude of the tunneling spin polarization (TSP) from ferromagnetic metals has received much attention in recent years. In particular, the relationship of the TSP to the magnetization of the magnetic material has been of considerable debate. Nearly all measurements to date have reported positive TSP values: these include all the 3d transition-metal ferromagnets [7–9] and their alloys as well as all the heavy rare-earth metals [10]. Negative TSP has been measured only in two ferromagnetic oxides, SrRuO₃ [11] and Fe₃O₄ [12], and has been inferred in a small number of cases from TMR studies [13–15].

Here we show, using superconducting tunneling spectroscopy that alloys of heavy rare-earth (RE) and ferromagnetic 3d transition metals (TM) can exhibit both significant positive and negative spin polarizations depending systematically on the composition of the alloy and that,

moreover, nominally zero magnetization alloys display large tunneling spin polarization.

The junctions were prepared at ambient temperature on Si(100) substrates covered with 250 Å SiO₂ using magnetron sputtering in a high vacuum deposition system with an *in situ* automated shadow-masking capability with typical junction areas of $\sim 80 \times 80 \mu\text{m}^2$. RE-TM alloys formed from Gd and Tb and from Co and Fe were studied, but detailed results are presented only for Co-Gd alloys. The Al₂O₃ barriers are formed either by reactive sputtering of Al in an Ar/O₂ mixture (yielding an Al₂O₃ film that is about 25 Å thick) or by plasma oxidation of an ~ 14 Å thick Al film and are amorphous. The MgO barriers are formed by reactive magnetron sputtering in an Ar-O₂ mixture [6] and, by contrast, are crystalline and highly (100) textured. The superconducting electrode in the STS samples was formed from Al₉₆Si₄, ~ 45 –60 Å thick, which was deposited either below or above the tunnel barrier. These are referred to as normal (n-FIS) and inverted (i-FIS) structures, respectively [16]. The n-FIS structures have ~ 300 Å thick Co-Gd alloy electrodes deposited on top of the tunnel barrier, whereas the i-FIS samples have a Co-Gd layer, 35–100 Å thick, grown beneath the barrier on underlayers of ~ 100 Å Ta/250 Å Ir₂₂Mn₇₈. The Co-Gd alloys are sputtered from alloy targets. Since the alloy composition in the deposited films can be varied from that of the target material by varying the sputtering gas pressure (higher pressures give higher Gd contents), the composition of the films was determined by Rutherford backscattering spectrometry on ~ 500 Å thick films protected from oxidation by a Ta layer, ~ 100 Å thick.

The MTJs for the temperature dependent measurements were fabricated with an MgO tunnel barrier, an exchange biased lower ferromagnetic electrode of Co-Fe (100 Å Ta/250 Å Ir₂₂Mn₇₈/35 Å Co₇₀Fe_{30-x}) and an upper Co-Gd counterelectrode, which was capped with 100 Å Ta. The magnetic properties of the samples were

studied using SQUID and vibrating sample magnetometry. All the RE-TM films exhibited an in-plane uniaxial magnetic anisotropy, although it is well known that such films can display either in-plane or perpendicular anisotropy depending on the deposition parameters [17]. Sputter-deposited RE-TM alloys are amorphous when deposited at room temperature with crystallization temperatures well above room temperature [17].

Figure 1 shows conductance versus applied voltage curves for several FIS structures with $\text{Co}_{1-x}\text{Gd}_x$ electrodes and x varying from 0 to 1. The measurements were made at ~ 0.25 K in a field of 2 T applied along the easy axis in the sample plane. In such STS studies a thin superconducting layer acts as a near perfect spin analyzer for the tunneling current due to the magnetic field induced Zeeman splitting of the superconductor quasiparticle density of states, so giving rise to 4 peaks in the conductance curves [7]. The spin polarization of the tunneling current leads to an asymmetry in the magnitude of these peaks for positive and

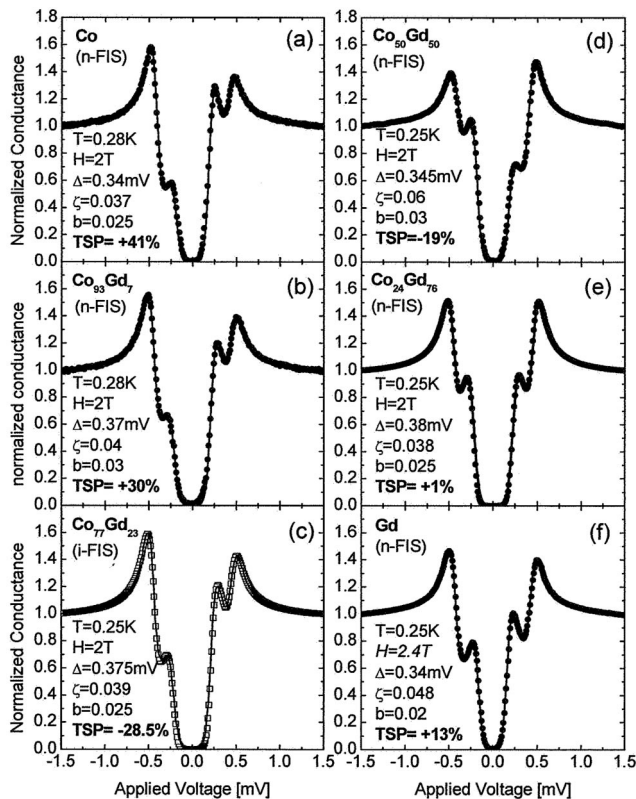


FIG. 1. Conductance curves for STS structures using Co-Gd electrodes of various compositions. ● and □ indicate data for samples with Al_2O_3 barriers and MgO barriers, respectively, and the solid line fits to the data using the density of states derived by Maki [18]. The type of structure is indicated in the graphs (i-FIS for inverted and n-FIS for normal structures). Both structures use the same voltage convention (bottom electrode is positive voltage). The fitting parameters are indicated as follows: superconducting gap Δ , depairing parameter ζ , spin-orbit parameter b , and tunneling spin polarization TSP. The temperature T and applied magnetic field H were those measured except for the field in the case of (f).

negative bias voltages. Each of the curves in Fig. 1 is measured with the bottom electrode positively biased, so that the asymmetry is reversed when the TSP changes sign or the FIS structure is inverted from the normal to the inverted phase. The TSP is extracted by fitting these curves using a quasiparticle density of states calculated according to the Maki theory [18] with fitting parameters of the superconducting energy gap Δ , an orbital depairing parameter ζ , and a spin-orbit scattering parameter b , and by using the measured temperature and field values. In agreement with previous reports, we find positive TSP (i.e., majority spin-polarized current) for both Co (+41%) [8] and Gd (+13%) [10]. Note that for Gd the conductance data can be fit only by using a field of ~ 2.4 T, which is significantly larger than the applied field. Previous studies have shown that rare-earth metals can give rise to significant proximity exchange fields in superconductors [19].

The detailed dependence of TSP on the Co-Gd alloy composition is summarized in Fig. 2(a). As the Gd content is increased, the TSP, which is positive for small Gd concentrations, changes sign and becomes negative at ~ 20 at. % Gd and remains negative for up to ~ 75 at. % Gd. For higher Gd concentrations the TSP is positive. The maximum negative TSP values of $\sim -30\%$ are found in the i-FIS structures with MgO tunnel barriers for Gd concentrations of ~ 20 –30 at. %. This is likely due to an improved interface quality for this inverted structure.

While there have been no studies to date of the TSP of RE-TM alloys, their magnetic and magneto-optical properties have been extensively researched [20,21]. It has been found that many properties of alloys containing the heavy REs (Gd to Tm) can be explained by assuming that there are substantially ferromagnetically aligned independent subnetwork magnetizations of the RE and TM moments, respectively, which are coupled antiparallel to one another. For Co-Gd alloys since, at low temperatures, the Gd magnetic moment ($\sim 7\mu_B$) is much larger than that of Co ($1.6\mu_B$), the RE subnetwork moment compensates that of the TM subnetwork at only ~ 20 at. % Gd. The abrupt change in sign of TSP that we observe at $\sim 20\%$ Gd thus coincides with the known compensation concentration of Co-Gd alloys. At this concentration the alloy films have nearly zero magnetization as shown in Fig. 2(b) in which their magnetization (at 10 K) is plotted versus Gd composition. The plot includes the highest magnetization values obtained. However, for compositions with more than $\sim 50\%$ Gd some films showed lower magnetization values, most likely due to Ar incorporation at higher sputter pressures. The dependence of the magnetization on Gd content is, otherwise, in very good agreement with prior work [22], as shown by the solid lines in the figure.

The dependence of TSP on composition can be understood qualitatively by considering a simple model in which the measured tunneling current is the sum of independent spin-polarized tunneling currents from the Co and Gd subnetworks, respectively. Support for such a model comes from scanning tunneling microscopy studies in which it is

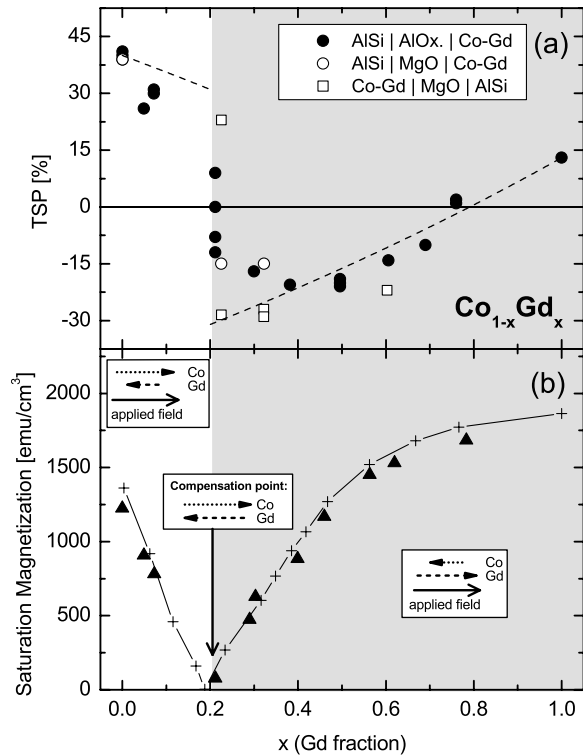


FIG. 2. (a) Tunneling spin polarization and (b) saturation magnetization versus Gd composition for $\text{Co}_{1-x}\text{Gd}_x$ alloys. In (a) the filled circles correspond to Al_2O_3 barriers while the open symbols correspond to MgO barriers in either normal (circles) or inverted (squares) structure. In (b) the solid triangles correspond to SQUID measurements at 10 K of the magnetization of ~ 1000 Å thick films of the respective Co-Gd alloys which were sandwiched between ~ 100 Å thick Ta layers to prevent oxidation. The crosses in (b) are from Ref. [22]. Insets of (b) show the alignment of the Co and Gd subnetwork magnetizations with respect to the applied field as a function of composition and the composition where compensation occurs, and the net magnetization vanishes (compensation point).

observed that the tunneling current can vary widely between neighboring atomic sites in metallic alloys [23]. The sign of the polarization of the tunneling currents depends on the orientation of the respective subnetwork magnetization with respect to the applied field. The TSP from either of these subnetworks will be positive when its magnetization is aligned with the applied magnetic field based on the observation that both the pure elements, Co and Gd, exhibit positive TSP (i.e., predominantly majority spin electrons taking part in the tunneling process). The magnetic moments of the subnetwork with the higher magnetization, which depends on the composition and the respective Co and Gd moments, will be oriented parallel to the applied field, so that the moments of the other subnetwork will consequently be antiparallel to the field, as shown schematically in the insets of Fig. 2(b). This latter subnetwork will then give rise to *negatively* spin-polarized current. Since the magnetic moment of Gd is much larger than that of Co but the TSP, by contrast, is much smaller

from Gd than from Co, this means paradoxically that for Gd concentrations just larger than the compensation concentration the net tunneling current displays a net negative spin polarization, as we observe. Eventually, when the Gd concentration is sufficiently large, the small positive TSP of the larger Gd current overcomes the much larger negative TSP of the smaller Co subnetwork current so that the TSP of the net current becomes positive as shown in Fig. 2(a).

Thus, we can model the polarization P of the tunneling current from the $\text{Co}_{1-x}\text{Gd}_x$ alloy system as $P = \text{sgn}(x_c - x)[P_{\text{Co}} \frac{1-x}{1-x+x/r} - P_{\text{Gd}} \frac{x}{x+(1-x)r}]$ where P_{Co} and P_{Gd} are the polarizations of the current from pure Co and Gd, respectively, x_c is the compensation concentration (~ 0.21), and r is the ratio of the tunneling probability from the Co as compared to the Gd sites. This formula can reasonably well account for the experimental observations as shown by the dashed line in Fig. 2(a) using values of $P_{\text{Co}} = 0.40$ and $P_{\text{Gd}} = 0.13$ and a tunneling probability that is $\sim 20\%$ higher from the Co sites than from the Gd sites (i.e., $r = 1.2$). The higher tunneling probability from the Co sites may be due to a number of factors, including the smaller size of Co compared to Gd, their different electronic structure, or the differences in bonding at the tunnel barrier interface [24]. At x_c this model predicts an abrupt change in sign of TSP from positive to negative values as the Co subnetwork magnetization switches its orientation from parallel to antiparallel to the applied field. Not surprisingly, we find a wide distribution of TSP values at this compensation concentration, since the orientation of the Co subnetwork magnetization is likely to be sensitive to small variations in the Gd concentration (due, for example, to inhomogeneities in the deposition process or sputter target).

For Gd concentrations that are slightly higher or lower than x_c , the measured TSP is large and is negative or positive, respectively. By contrast, the magnetization of these alloys is small [see Fig. 2(b)]. For example, $\text{Co}_{77}\text{Gd}_{23}$ exhibits a TSP of $\sim -29\%$, but its magnetization is more than 10 times lower than that of pure Co. Thus we conclude from these experiments that it is possible to develop magnetic alloys with vanishingly small magnetization yet with sizable tunneling spin polarization. Such materials would be very useful for device applications because they would eliminate magnetic dipole fields that can give rise to significant magnetic coupling within and between devices [4]. This property exhibited by Co-Gd alloys should also be common to many other RE-TM alloy systems: indeed, we find similar behavior in CoTb and FeTb alloys. A common feature of these alloys is that only a relatively small concentration of the high moment RE is needed to magnetically compensate the lower moment TM so that the tunneling current is dominated by that from the highly polarized TM atoms.

The TSP can be determined from STS studies only at low temperatures below the superconducting transition

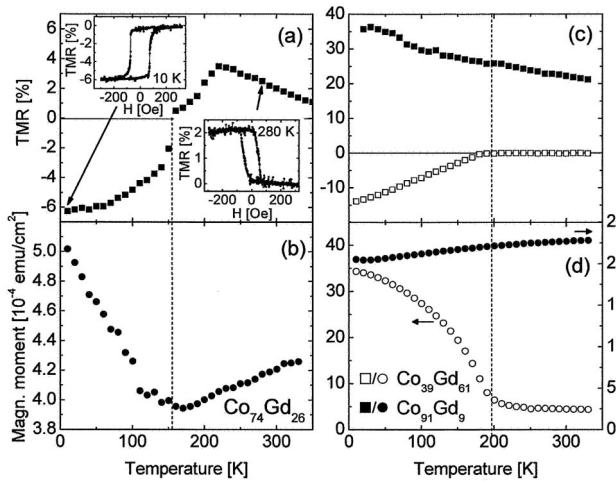


FIG. 3. Temperature dependence of Co-Gd electrode saturation magnetization and TMR of tunnel junctions with exchange biased $\text{Co}_{70}\text{Fe}_{30}$ electrodes and a counterelectrode of (a) and (b) 43 Å $\text{Co}_{74}\text{Gd}_{26}$, and (c) and (d) 300 Å $\text{Co}_{91}\text{Gd}_9$ and 330 Å $\text{Co}_{39}\text{Gd}_{61}$. Note that the crossover in sign of TMR and the magnetization minimum occur at the same temperature (~ 150 K). Insets in (a) show examples of TMR versus field plots for negative and positive TMR.

temperature of the AlSi electrode. The temperature dependence of the TSP can, however, be inferred from the tunneling magnetoresistance of MTJs with a RE-TM electrode and a counterelectrode formed from a conventional TM ferromagnet whose TSP is positive and varies little with temperature. In particular, following Julliere's model [1], the TMR is positive or negative when the TSP of the RE-TM electrode is positive or negative, respectively.

The temperature dependence of the TMR and corresponding saturation magnetization of an MTJ with a 43 Å thick $\text{Co}_{74}\text{Gd}_{26}$ electrode and an exchange biased $\text{Co}_{70}\text{Fe}_{30}$ counterelectrode [4] are shown in Figs. 3(a) and 3(b). Consistent with the negative TSP found from STS measurements for this alloy the TMR is negative at low temperatures. However, as the temperature is increased, the magnitude of the TMR decreases and abruptly changes sign to become positive at ~ 150 K. The magnetization of the MTJ exhibits a minimum value at this same temperature. These features are consistent with a compensation of the Co and Gd subnetwork magnetizations at this temperature, which results from the stronger temperature dependence of the Gd subnetwork compared to that of the Co subnetwork magnetization [25,26]. Data are also shown in Figs. 3(c) and 3(d) for MTJs with CoGd electrodes with both smaller and larger Gd concentrations such that the Co and Gd subnetwork magnetizations, respectively, are dominant over the temperature range for which TMR was measured. In the latter case the Gd content is so high that the Curie temperature is below room temperature.

In summary, we have demonstrated that Co-Gd alloys can exhibit both positive and negative tunneling spin polarizations depending on their composition and the tempera-

ture. Similar results have been obtained for alloys of Co and Fe and of Gd and Tb. This unusual property derives from the ferrimagnetic structure of these alloys and can be understood as a consequence of a much higher polarization of the tunneling current from the transition metal as compared to the rare-earth-metal component and the much higher magnetic moment of the latter. An interesting consequence is that alloys at the temperature dependent compensation concentration can exhibit zero magnetization but give rise to strongly spin-polarized current.

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- [1] M. Julliere, Phys. Lett. **54A**, 225 (1975).
- [2] J. S. Moodera *et al.*, Phys. Rev. Lett. **74**, 3273 (1995).
- [3] T. Miyazaki and N. Tezuka, J. Magn. Magn. Mater. **139**, L231 (1995).
- [4] S. S. P. Parkin *et al.*, Proc. IEEE **91**, 661 (2003).
- [5] D. Wang *et al.*, IEEE Trans. Magn. **40**, 2269 (2004).
- [6] S. S. P. Parkin *et al.*, Nat. Mater. **3**, 862 (2004).
- [7] R. Meservey and P. M. Tedrow, Phys. Rep. **238**, 173 (1994).
- [8] D. J. Monsma and S. S. P. Parkin, Appl. Phys. Lett. **77**, 720 (2000).
- [9] B. Nadgorny *et al.*, Phys. Rev. B **61**, R3788 (2000).
- [10] R. Meservey, D. Paraskevopoulos, and P. M. Tedrow, J. Appl. Phys. **49**, 1405 (1978).
- [11] D. C. Worledge and T. H. Geballe, Phys. Rev. Lett. **85**, 5182 (2000).
- [12] A. F. Panchula, Ph.D. thesis, Stanford University, Stanford, 2003.
- [13] M. Sharma, S. X. Wang, and J. H. Nickel, Phys. Rev. Lett. **82**, 616 (1999).
- [14] J. M. De Teresa *et al.*, Science **286**, 507 (1999).
- [15] C. Mitra *et al.*, Phys. Rev. Lett. **90**, 017202 (2003).
- [16] C. Kaiser and S. S. P. Parkin, Appl. Phys. Lett. **84**, 3582 (2004).
- [17] P. Hansen, in *Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, Landolt-Bornstein New Series (Springer-Verlag, Berlin, 1988), Vol. 19g, p. 136.
- [18] D. C. Worledge and T. H. Geballe, Phys. Rev. B **62**, 447 (2000).
- [19] J. E. Tkaczyk and P. M. Tedrow, J. Appl. Phys. **61**, 3368 (1987).
- [20] P. Hansen, J. Magn. Magn. Mater. **83**, 6 (1990).
- [21] P. Hansen, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier Science, Amsterdam, 1991), Vol. 6, p. 289.
- [22] P. Hansen *et al.*, J. Appl. Phys. **66**, 756 (1989).
- [23] W. A. Hofer, A. S. Foster, and A. L. Shluger, Rev. Mod. Phys. **75**, 1287 (2003).
- [24] C. Kaiser, S. van Dijken, S.-H. Yang, H. Yang, and S. S. P. Parkin, Phys. Rev. Lett. **94**, 247203 (2005).
- [25] P. Chaudhari, J. J. Cuomo, and R. J. Gambino, Appl. Phys. Lett. **22**, 337 (1973).
- [26] K. Moosjani and J. M. D. Coey, *Magnetic Glasses* (Elsevier, Amsterdam, 1984).