PHYSICAL REVIEW B, VOLUME 64, 100406(R)

Sign reversal of spin polarization in Co/Ru/Al_2O_3/Co magnetic tunnel junctions

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(Received 21 February 2001; published 22 August 2001)

Utilizing ultrathin Ru interfacial layers in Co/Al_2O_3/Co tunnel junctions, we demonstrate that not only does the tunnel magnetoresistance decrease strongly as the Ru thickness increases as found for Cu or Cr interlayers, in contrast, even the sign of the apparent tunneling spin polarization may be changed. Further, the magnitude and sign of the apparent polarization is strongly dependent on applied voltage. The results are explained by a strong density-of-states modification at the (interdiffused) Co/Ru interface, consistent with theoretical calculations and experiments on Co/Ru metallic multilayers and Co-Ru alloys.

DOI: 10.1103/PhysRevB.64.100406 PACS number(s): 75.70.−i, 73.40.Gk, 85.30.Mn, 85.70.Kh

The recent discovery of large magnetoresistance in magnetic tunnel junctions[1] (MTJ's) has initiated a large amount of research into these structures, both from a technological and fundamental viewpoint. From the fundamental point of view, the sensitivity of these structures to the exact nature of the ferromagnet-insulator interface(s)[2–7] is intriguing. In order to investigate this interfacial sensitivity, experiments utilizing ultrathin metallic layers inserted at the ferromagnet-insulator interface[4–6,8,9] have proven insightful. Some of these experiments have proven difficult to interpret due to growth-related artifacts.[9] Previously, using Cr[6] and Cu[8] interfacial layers in Co/Al_2O_3/Co junctions, we have demonstrated the key role of the density of states at the ferromagnet-insulator interface in determining the properties of these junctions. Specifically in the case of junctions with Cr interlayers,[6] the strong decrease of the TMR with Cr thickness (reduced by 80% for 1 monolayer Cr) as well as the unusual conductance-voltage properties could be qualitatively explained by considering the density of states alteration due to spin-dependent band matching at an (interdiffused) Co/Cr interface with spin-fluctuating Cr moments. Although the Tunnel Magnetoresistance (TMR) decreased extremely rapidly for Cu and Cr interlayers, it remained *positive* for all interlayer thicknesses studied.

In this communication, we present TMR as a function of Ru interlayer thickness and applied dc bias, and show that not only may the apparent tunneling spin polarization be strongly reduced at Co-Ru interfaces, as with Co-Cr interfaces, its sign may be reversed as well. In contrast to Cr interlayers, where zero-bias conductance anomalies (attributed to fluctuating Cr moments) were observed for all Cr thicknesses, with Ru interlayers the anomalies were only observed for Ru thicknesses much less than 1ML.[10] Zero-bias conductance anomalies *were not observed when the apparent Co/Ru polarization was negative*, suggesting that the negative polarization results purely from a density-of-states modification. Further, structural characterization of the Co-Ru interfaces utilizing ^{59}Co NMR indicates significant interdiffusion, and essentially precludes an explanation based on quantum well states.[11] The negative apparent spin polarization is in qualitative agreement with the density of states modification expected based on local density of states calculations,[12–14] spin-resolved photoemission experiments,[15] and transport in Co-Ru multilayers[13,14,16] and alloys.[17]

Ferromagnetic tunnel junctions were prepared by UHV dc/rf magnetron sputtering (base pressure $<5\times10^{-10}$ mbar) through metal contact masks onto plasma oxidized Si(100) substrates. The details of this fabrication process have been described elsewhere.[8,18] The TMR structures used consisted of: Si(001)/SiO_2/Ta 50 Å /Co 70 Å /FeMn 100 Å /Co 35 Å /Al_2O_3/Co 150 Å /Al 30 Å postannealed in a magnetic field at 200 °C for 30 min to establish a uniform exchange biasing direction. The Al_2O_3 barrier was formed by plasma oxidation of 23 Å Al. Dusting layers were inserted at the *bottom* Co/Al_2O_3 interface[8] to avoid spurious effects due to clusterlike growth at the top Al_2O_3 interface. *In situ* XPS and differential ellipsometry were used to confirm that there was no electrode or dusting layer oxidation, with a minimal amount of remaining metallic Al.[8,19] Junction resistances and conductances $[dI/dV\equiv G(V)]$ or dynamic resistances $[dV/dI=G^{-1}(V)]$ were measured using standard ac lock-in techniques ($f=1.01$ kHz), at 10 K with the ac excitation kept well below k_BT to avoid modulation broadening. TMR ($\Delta R/R_p$ or $\Delta G/G_a$) was measured using both dc and ac lock-in techniques.

Figure 1 shows the normalized TMR vs Ru thickness at 10 K. As with Cr interlayers, the normalized TMR decreases extremely rapidly for the first monolayer (1 ML$\approx$2 Å) of Ru coverage. In striking contrast to Cr[6] or Cu[8] interlayers, however, beyond approximately 1ML Ru coverage the TMR *reverses sign*, i.e., the TMR is negative. Until about 1ML of nominal Ru coverage, the decay of TMR with Ru thickness is approximately as rapid as for Cr interlayers. However, for Cr interlayers, *the TMR always remained positive* up to 3 ML ($\sim$6 Å) nominal Cr thickness. Previously, a sign reversal of the TMR was observed by de Teresa *et al.*[5] and Sharma *et al.*[7] using *composite insulating barriers*, which is not relevant for the present case. Worledge and Geballe[20] observed negative polarization with $SrRuO_3$, which was explained in terms of the bulk band structure of that compound and not in terms of any interfacial effects. A negative TMR was also observed by Moodera *et al.*[11] utilizing Au interlayers on Co. In that case, the negative TMR was explained by the formation of (spin-dependent) quantum well (QW) states in the Au

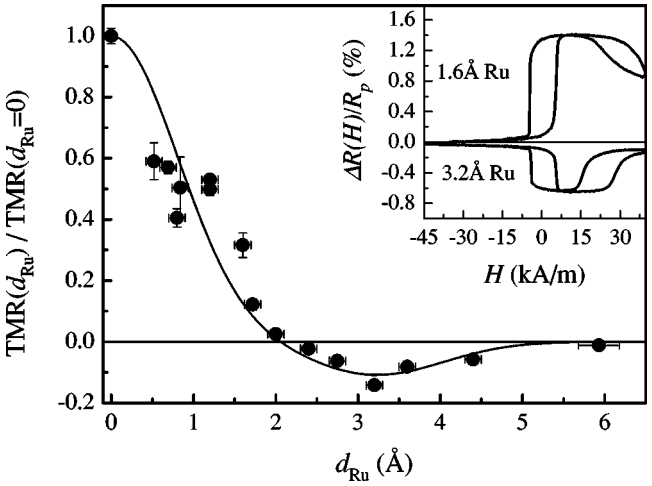

FIG. 1. Normalized TMR at 10 K as a function of Ru interlayer thickness (see text for structural description). The line is only a guide to the eye. Inset: Resistance vs applied field for a control junction, and junctions with 1.6 and 3.2 Å Ru.

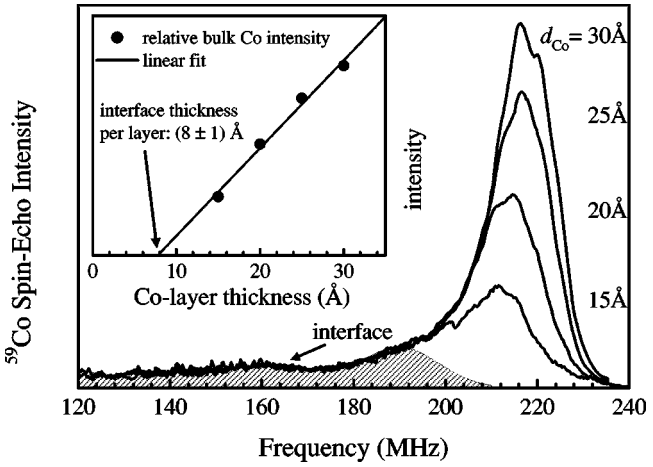

FIG. 2. ^{59}Co NMR spectra for Co/Ru multilayers for different Co thicknesses [$5\times(d_{Co}$ Co+10 Å Ru)]. Shaded area represents the interface contribution. Inset: the relative bulk Co intensity as a function of Co thickness.

layer. However, coherent electron transport, and hence QW state formation, in the Ru requires sharp Co/Ru and Ru/Al_2O_3 interfaces, as well as an extremely uniform (and typically single-crystalline) interlayer. Thus, for an explanation based on QW state formation to be applicable, as opposed to, e.g., in terms of the density of states of an *intermixed* Co-Ru interface, structural characterization is an important burden of proof.

From various structural investigations on Co/Ru multilayers,[21] a rather large amount of interdiffusion is expected at the Co/Ru interface ($\sim$2 ML). The presence of a relatively broad, interdiffused interface[21] would essentially preclude an explanation based on QW states in the Ru layer, and favor an explanation based on the electronic properties of Co-Ru alloys and interfaces. To this end, we have performed ^{59}Co Nuclear Magnetic Resonance (NMR) measurements on separately grown Co/Ru multilayers, sputtered under identical conditions. Multilayers were used only to increase the signal to noise ratio. NMR measurements give information on the distribution of different local environments of Co atoms by directly probing the hyperfine field at the Co nuclei. From this distribution of hyperfine fields it is possible to distinguish ''bulk'' (Co atom with only Co neighbors) and ''interface'' (Co atoms with non-Co neighbors) Co atoms and to determine their relative amounts.[22,23] NMR experiments were performed at 1.5 K in zero-applied field with frequencies between 120 and 240 MHz on multilayers consisting of 35 Å Ru+$5\times(d_{Co}$Co+10 Å Ru)+12 Å Ru, with d_{Co}=15, 20, 25, and 30 Å. The spectra are corrected for the frequency dependence of the ferromagnetic enhancement factor and power absorption. The resulting spectra for the different Co thicknesses as well as the relative ''bulk'' Co intensity as a function of d_{Co} are shown in Fig. 2. It can be seen that the relative ''bulk'' Co intensity becomes 0 for a Co-layer thickness of 8 ± 1 Å, meaning that per interface, 2.0 ± 0.2 ML of Co have at least one Ru neighbor, i.e., the Co/Ru interface is interdiffused. In a more detailed analysis, the distribution of Co hyperfine fields is fitted using a gradual transition from a pure Co-layer to a pure Ru-layer with a few mixed interface layers of varying Co concentrations.[21] From this it is found for that at least 3.5 ± 1 Å of Ru on Co, the topmost layer is a mixed layer and that for the first 4.6 ± 0.5 Å of Ru, all Ru-atoms have Co neighbors. Though the exact number of mixed layers depends on the details of the interface model used,[21] it is clear that even lower-bound estimates indicate that at the thickness for zero-crossing of the TMR, all Ru present has some Co neighbors, *i.e., we may consider the dusting layer as a Co-Ru interface alloy whose composition varies with nominal Ru thickness* (though we will continue to refer to nominal Ru thicknesses for convenience). Finally, we note that although the multilayers used for NMR measurements were unannealed, TMR results were similar for annealed or unannealed samples.

One trivial explanation for the negative TMR is that the Co-Ru interface alloy is antiferromagnetically (AF) coupled to the ''bulk'' Co, leading to an inversion of the usual TMR and hence an *apparent* negative polarization. However, several observations make this explanation unlikely. If an AF coupled surface layer were present, a further resistance change should be observed at fields approaching and beyond the AF coupling strength. However, TMR was measured in fields up to 8 T for various Ru thicknesses with negative TMR, and *no further change in resistance was observed*. Further, the striking similarity to results by Moodera *et. al.*[11] using Au interlayers in Co based junctions, where no strong AF coupling[24] or interface alloy is expected for the thicknesses used, also suggests that this is a more general phenomenon which requires an explanation based on electronic structure. Given the intermixed nature of the Co/Ru interface, we feel that an explanation based on QW states is unlikely. Finally, if the reversed TMR is purely magnetic in origin, i.e., no strong density of states modification, no unusual bias dependence would be expected in these structures. The bias dependence of the TMR observed is, we believe,

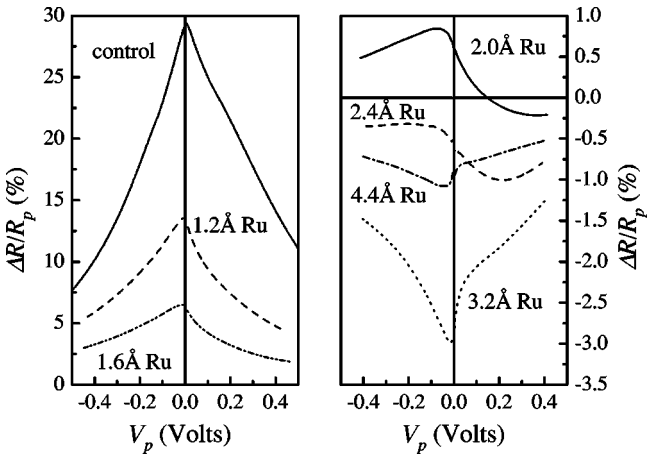

FIG. 3. TMR as a function of applied dc bias at 10 K. Left panel: 0, 1.2, and 1.6 Å Ru dusting layers. Right panel: 2.0, 2.4, 3.2, and 4.4 Å Ru dusting layers. Note the change in vertical axis scale for the right panel.

crucial to elucidating the likely explanation of the unusual behavior displayed in these junctions and will be discussed presently.

As mentioned previously,[6] an explanation based on Ru impurities in Co (or vice versa) and spin-dependent band matching may be more reasonable to explain the present data. In this case, a strongly altered density of states may be expected to manifest itself in the TMR-voltage characteristics. Indeed, near and beyond the sign reversal of the TMR, an unusual dc bias dependence of the TMR is exhibited. Shown in Fig. 3 is the TMR as a function of applied dc bias for a control junction and several thicknesses of Ru interlayers. We note that the bottom electrode (i.e., the Ru dusted electrode) is biased positively for $V>0$. For typical Co-Al_2O_3 junctions, the TMR decreases approximately linearly with bias in the range of ~ 0.5 V, and is nearly symmetric,[18] as for the control junction. With only 1.2 Å nominal Ru coverage, the bias dependence is already noticeably nonlinear, but still approximately symmetric. By 1.6 Å Ru, however, the bias dependence has become asymmetric, with a stronger decrease for positive voltages. At 2.0 Å Ru, near the zero crossing of the zero-bias TMR, the bias dependence is not only strongly asymmetric, but the TMR becomes *negative* for $V>0.15$ V, while remaining positive for all lower voltages. With only an additional 0.4 Å Ru, beyond the zero-crossing of the zero-bias TMR, the bias dependence for 2.4 Å Ru is mirrored about the voltage and magnetoresistance axes, and the TMR remains negative for all biases. For larger thicknesses (3.2 and 4.4 Å Ru), the bias dependence becomes slightly more symmetric, but with a faster decrease of magnetoresistance for positive bias. For Ru thicknesses slightly below the zero-crossing point of the TMR, positive zero-bias TMR could become negative by applying a positive voltage. On the other hand, for slightly larger Ru thicknesses, *negative zero-bias TMR remained negative for any applied voltage*. While a positive TMR can be driven negative by increasing bias or increasing Ru thickness, a negative TMR cannot be driven positive again, at least within the available ± 1V. Qualitatively, it seems that applying a positive bias is essentially the same as increasing the Ru thickness (or Ru concentration of the Co_xRu_{1-x} interface alloy), suggesting perhaps an explanation based on the changing density of states of the Co-Ru interface alloy with increasing Ru concentration. This further indicates that the negative TMR cannot be explained by an AF coupled interface alloy, as in that case the bias dependence should be simply mirrored about the voltage axis. Further, the sign reversal with an applied positive bias for some Ru thicknesses would not be explained.

In order to relate the dependence of the TMR on Ru thickness or applied bias voltage to the density of states of the Co-Ru interfacial alloy, it must be clarified *which* density of states is relevant for tunnel conductance in these structures. Gadzuk[25,26] pointed out that despite the fact that at the Fermi energy *d* states are far more numerous in, e.g., Co, the more mobile *s* electrons dominate the tunnel current. In this way, the measured *positive* (i.e., majority) tunneling spin polarization[2] could be explained. This simple explanation has been borne out recently by more sophisticated treatments of MTJ's. Tsymbal and Pettifor[27,28] emphasized electrode-barrier interface bonding, and found that when only *s*-*s* bonding is taken into account, the correct magnitude and sign of the spin polarization may be accounted for in Fe and Co. Butler *et al.*[29] have performed *ab initio* calculations for Fe-MgO-Fe junctions, also finding the tunnel current is *s* dominated. Due to *s*-*d* hybridization, a high *d* density of states at E_F necessarily leads to a low *s* density of states at E_F.

For Cr interlayers,[6] the polarization decrease was explained in terms of the mismatch between the majority-spin *d* levels of Co and Cr, which prevents hybridization of these bands. The resonant scattering of majority spin *s*-*p* electrons with Cr *d* states results in the majority spin density of states becoming highly localized at Cr sites (i.e., the formation of a virtual bound state leads to a high majority spin density of states near the Fermi level on Cr sites). As expected, the *s*-*p* density of states is then suppressed for majority spins and strongly decreases the polarization. For Ru interfaces with Co, or impurities in Co, an even larger scattering cross section and spin asymmetry is expected,[30] and hence an even larger modification of the interfacial density of states.[12,13,17] Calculations of the density of states for various Co-Ru alloys have been previously performed by Rahmouni *et al.*,[14] which indicate that between approximately 8–16 % Ru indeed the sign of the *total* polarization, dominated by *d* states, indeed changes sign. Following the notion that the *s* polarization should track the *d* polarization inversely, one may also reasonably expect that the *s* polarization changes sign as well. As a rough approximation, the effect of adding Ru to the alloy appears to shift the majority density of states to higher energies, while doing little to the minority bands.

Combining these notions with our observations, we may hypothesize that the negative zero-bias TMR results from gradually changing the interface from pure Co, with a positive *s* spin polarization, to a dilute Co-Ru alloy, which above a critical composition has a *negative s* polarization, consistent with density of states calculations,[12–14] dilute alloy studies,[17] and giant-magnetoresistance measurements.[14,16]

For higher concentrations of Ru, the interface alloy becomes nonmagnetic, and thus, tends toward zero polarization. By considering the shifting of the majority band to higher energies with increasing Ru concentration, the unusual dc bias dependence may also be explained. For positive bias, the conductance reflects the density of states, and thus polarization, *above* E_F of the Co-Ru alloy. At energies above E_F for a given Ru composition, a strong polarization decrease with increasing energy may be expected, as observed. At Ru concentrations near but below that required for a negative zero-bias polarization, a slight positive bias may decrease and invert the polarization, but a negative polarization cannot become positive again with applied bias. Further, since increasing Ru concentration shifts the majority density of states higher in energy, we may speculate that increasing Ru thickness and a positive dc bias are expected to have a similar effect on the sp polarization. Though the gross features of the Co-Ru alloy density of states correlate favorably with the observed TMR thickness and bias dependence, more detailed calculations of the sp local density of states for Co-Ru alloys are necessary to completely verify this explanation. Finally, we point out that *despite* the fact that an explanation based on QW state formation is essentially precluded in this case by structural characterization, a striking resemblance to the results of Moodera *et al.*[11] with Au interlayers remains. We propose that perhaps these results may be in need of reinterpretation as well, and can perhaps be better explained in terms of the density of states modification at Co-Au interfaces.

In conclusion, using ultrathin Ru interfacial layers in $Co/Al_2O_3/Co$ tunnel junctions, we demonstrate that the sign of the effective spin polarization of the Co/Ru electrode may be changed. Unlike other experiments demonstrating a negative effective spin polarization, we may effectively rule out quantum well states or interface bonding as likely explanations. The negative polarization is explained by a strong density of states modification at the Co/Ru interface, which may be considered an interface alloy, consistent with giant magnetoresistance and dilute alloy transport experiments and Co-Ru alloy density of states calculations. Considered in the proper light, properties of dilute alloys and giant magnetoresistance multilayers can provide key insights into transport in magnetic tunnel junctions. These results demonstrate the possibility of systematically altering the properties of magnetic tunnel junctions via an engineered interfacial density of states, perhaps for improved device properties.

The authors would like to acknowledge R. Coehoorn and K. Flipse for valuable discussions and comments and C. H. van de Vin for assistance in transport measurements. P. LeClair was supported by the Netherlands technology foundation STW.

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[1] J. S. Moodera, L. R. Kinder, T. M. Wong, and R. Meservey, Phys. Rev. Lett. **74**, 3273 (1995).

[2] R. Meservey and P. M. Tedrow, Phys. Rep. **238**, 173 (1994).

[3] J. S. Moodera, J. Nassar, and J. Mathon, J. Magn. Magn. Mater. **200**, 248 (1999).

[4] J. S. Moodera, T. H. Kim, C. Tanaka, and C. H. de Groot, Philos. Mag. B **80**, 195 (2000).

[5] J. M. de Teresa *et al.*, Science **286**, 507 (1999).

[6] P. LeClair, J. T. Kohlhepp, H. J. M. Swagten, and W. J. M. de Jonge, Phys. Rev. Lett. **86**, 1066 (2001).

[7] M. Sharma, S. X. Wang, and J. H. Nickel, Phys. Rev. Lett. **82**, 616 (1999).

[8] P. LeClair, H. J. M. Swagten, J. T. Kohlhepp, R. J. M. van de Veerdonk, and W. J. M. de Jonge, Phys. Rev. Lett. **84**, 2933 (2000).

[9] J. J. Sun and P. P. Freitas, J. Appl. Phys. **85**, 5264 (1999).

[10] The presence or absence of zero-bias anomalies is a sensitive function of the magnetic coupling between Co and Cr or Ru moments. A more detailed description of the conditions giving rise to anomalies will be the subject of a subsequent paper.

[11] J. S. Moodera *et al.*, Phys. Rev. Lett. **83**, 3029 (1999).

[12] V. S. Stepanyuk, R. Zeller, P. H. Dederichs, and I. Mertig, Phys. Rev. B **49**, 5157 (1994).

[13] H. Itoh, J. Inoue, and S. Maekawa, Phys. Rev. B **47**, 5809 (1993).

[14] K. Rahmouni *et al.*, Phys. Rev. B **59**, 9475 (1999).

[15] A. Rampe *et al.*, Phys. Rev. B **51**, 3230 (1995).

[16] C. Vouille *et al.*, Phys. Rev. B **60**, 6710 (1999).

[17] P. L. Rossiter, in *The Electrical Resistivity of Metals and Alloys* (Cambridge University Press, Cambridge, 1987).

[18] P. LeClair, H. J. M. Swagten, J. T. Kohlhepp, and W. de Jonge, Appl. Phys. Lett. **76**, 3783 (2000).

[19] P. LeClair *et al.*, J. Appl. Phys. **87**, 6070 (2000).

[20] D. C. Worledge and T. H. Geballe, Phys. Rev. Lett. **85**, 5182 (2000).

[21] P. Panissod, in *Frontiers in Magnetism of Reduced Dimension Systems*, edited by V. G. Bar'yakhtar, P. E. Wigen, and N. A. Lesnik (Kluwer Academic Publishers, Dordrecht, 1998), pp. 225–270.

[22] P. C. Riedi, T. Thomson, and G. J. Tomka, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 1999), Vol. 12, pp. 97–258.

[23] W. de Jonge, H. A. M. de Gronckel, and K. Kopinga, in *Ultrathin Magnetic Structures II*, edited by B. Heinrich and J. A. C. Bland (Springer-Verlag, Berlin, 1994), p. 279.

[24] J. J. de Vries, W. J. M. de Jonge, M. T. Johnson, J. aan de Stegge, and A. Reinders, J. Appl. Phys. **75**, 6440 (1994).

[25] J. W. Gadzuk, Phys. Rev. **182**, 416 (1969).

[26] E. L. Wolf, in *Principles of Electron Tunneling Spectroscopy* (Oxford University Press, London, 1985), Chap. 8.

[27] E. Y. Tsymbal and D. G. Pettifor, Phys. Rev. B **58**, 432 (1998).

[28] E. Y. Tsymbal and D. G. Pettifor, J. Phys.: Condens. Matter **9**, L411 (1997).

[29] W. H. Butler, X. G. Zhang, T. C. Schulthess, and J. M. MacLaren, Phys. Rev. B **63**, 054416 (2001).

[30] For example, in dilute Co-based alloys, the ratio of majority to minority spin resistivities is approximately 5 for Co-Cr alloys versus approximately 14 for Co-Ru alloys; see, e.g., Ref. 17.