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Zero-bias anomaly in ferromagnetic Ni nanoconstrictions

K. Ienaga,[1] N. Nakashima,[1] Y. Inagaki,[1] H. Tsujii,[2] S. Honda,[3] T. Kimura,[4] and T. Kawae[1,*]
[1]*Department of Applied Quantum Physics, Faculty of Engineering, Kyushu University, Motooka, Nishi-Ku, Fukuoka 819-0395, Japan*
[2]*Department of Physics, Faculty of Education, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan*
[3]*Organization for Research and Development of Innovative Science and Technology, Kansai University, Yamate, Suita 564-8680, Japan*
[4]*INAMORI Frontier Research Center, Kyushu University, Motooka, Nishi-Ku, Fukuoka 819-0395, Japan*

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We study the electrical conductance in a ferromagnetic Ni constriction, changing its size using a mechanically controllable break junction technique. A Fano resonance with a zero-bias anomaly, likely due to the Kondo effect, appears in Ni atomic-scale contacts and changes shape as the size of the contact changes. Moreover, the zero-bias anomaly persists in large size constrictions with nearly 50-atom configurations where the bulk ferromagnetic properties should be retained, despite the decrease of the signal intensity. The results suggest that the Kondo effect and ferromagnetism could coexist in the ferromagnetic nanoconstrictions.

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The Kondo effect is an important concept for understanding many intriguing phenomena in strongly correlated electronic materials, for example, heavy fermion,[1] heavy-fermion superconductivity,[2] and non-Fermi-liquid behavior.[3] It also accounts for characteristic behavior in the conductance of nanosystems such as lithographically defined semiconductors and molecular transistors.[4–7] All these phenomena are understood as the shielding of magnetic or quadrupolar moments by the surrounding conduction electrons,[8–10] implying that the Kondo effect competes with the itinerant-electron ferromagnetism.

Recently, the Kondo effect has been reported in atomic-size contacts fabricated from the ferromagnets Fe, Co, and Ni, where the two electrodes are made of pure ferromagnets by Calvo *et al.*[11] A Fano-Kondo resonance with a zero-bias anomaly is shown in the differential conductance for the atomic-size contacts prepared by scanning tunneling microscopy (STM) and electromigration. Moreover, the temperature dependence of the anomaly follows $-\ln T$ dependence. Their results suggest that when a ferromagnetic wire is reduced to the scale of a single atom, the conventional understanding of the Kondo effect must be modified.

In this paper we study the contact size dependence of a Fano resonance in a ferromagnetic Ni constriction using a mechanically controllable break junction (MCBJ) technique.[12] While the Ni wire is stretched at a very low speed in the final stage of breaking, typically taking a few hours, we measure the conductance and the differential conductance simultaneously. The differential conductance dI/dV is measured as a function of the bias voltage using a lock-in technique with $f = 1$ kHz. To reestablish the constriction after breaking the wire, the separate pieces of the wire are brought together to a distance of several nanometers. All procedures are performed at low temperatures to reduce thermal fluctuation and prevent contamination at the contact due to outgassing. By applying this method, we show that the Kondo effect would survive in large size constrictions where the bulk ferromagnetic properties is retained.

We have constructed a histogram of the conductance for 2000 conductance measurements in zero magnetic field as shown in Fig. 1. The peaks at around $1.7G_0$ and $3.2G_0$, where $G_0 = 2e^2/h$, are in good agreement with previous experiments obtained from thousands of counts and with theoretical predictions.[11,13] According to the Landauer formula, the conductance is given as $G = G_0\Sigma T_i$, where T_i is the transmission probability of the ith channel. Since in ferromagnetic Ni d electrons are involved in the conduction, the conductance is given by the sum of the conduction channels for the majority and minority spin components. Hence, the local properties, such as the spin polarization, change enormously because of the elongation of the constrictions in the final stage of the stretching, which makes the conductance trace complicated.[13] Indeed, the trace shows the deviation of the conductance plateau from the integer multiples of G_0 and the increase of the conductance despite the monotonic elongation of the Ni wire, as shown in the upper panel of Fig. 2(a).

We have recorded the dI/dV spectra in hundreds of breaking processes in Ni wires. Most of the dI/dV curves show peaks or dips around zero bias during the breaking process. In the lower panel of Fig. 2(a) we illustrate the continuous evolution of the dI/dV spectra in the final stage of breaking below $G(0) \leqslant 2G_0$, where $G(0)$ is the zero-bias conductance, that is, dI/dV at $V = 0$. All the dI/dV spectra exhibit a Fano-like resonance with a peak or dip shape anomaly at around zero bias, which changes its shape through the stretching of the constriction. The spectra are very similar to those observed in STM spectroscopy of single magnetic adatoms on nonmagnetic surfaces,[14] suggesting the appearance of Kondo resonance in atomic-scale contacts as reported by Calvo *et al.*[11] In particular, it is significant that the dI/dV spectra change gradually with the same conductance plateau with stretching of the constriction, while the shape of the zero-bias anomaly changes enormously at the jump of the conductance. Generally, the stretching causes a change of the electron energy level in the contact due to a change of the overlap of the wave function, so that the motion of the electrodes leads to a similar behavior as that observed in the gate-voltage effect in quantum dot systems.[15,16] Thus it is reasonable to consider that the evolution of the spectra is caused by variations of the electronic properties in the constrictions due to changes in the atomic configuration.

We can fit the dI/dV spectra to the sum of a background component g_0 and a Fano resonance given by the following

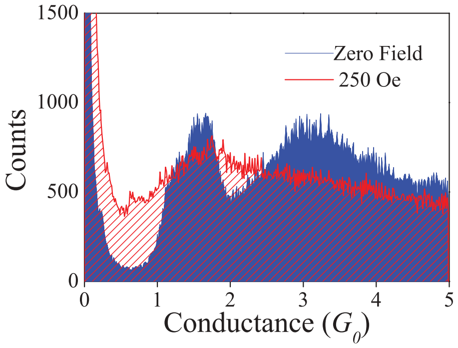

FIG. 1. (Color online) The histogram for about 2000 conductance measurements at $T \sim 5$ K in zero field and in a magnetic field of 250 Oe applied in parallel to the Ni wires.

equation:

$$\frac{1}{G_0}\frac{dI}{dV} \propto g_0 + \frac{A}{1+q^2}\,\frac{(q+\epsilon)^2}{1+\epsilon^2}. \tag{1}$$

Here $\epsilon = (eV - \epsilon_0)/k_B T_K$ is the bias shifted with respect to the center of the resonance ϵ_0, and normalized by the natural width of the resonance $k_B T_K$; k_B is Boltzmann's constant and T_K is a fitting parameter; q is the asymmetry parameter of the Fano theory and A is the amplitude of the signal. In the case that the resonance originates from the Kondo effect, T_K is taken as the Kondo temperature, as in previous studies.[11] Thus we discuss the origin of the Fano resonance below by referring to Calvo *et al.*[11] The best fits to the spectra are shown in Fig. 2(a). In atomic-scale constrictions, the resonance is nearly 20% to the total signal and T_K at each conductance step in Fig. 2(a) varies between 60 and 200 K. These values are somewhat smaller than those performed by STM,[11] but they are in reasonable agreement with those measured by the spear-anvil technique.[17] It is suggested from these results that the electronic and magnetic properties of the contact depends on how to prepare it.

Here we discuss the effects of an atomic-scale domain wall as the possible origin of the Fano resonance. It is known that a domain wall in ferromagnetic metals is a source of resistance.[18,19] Also, magnetoresistance effects are observed in the Fano-resonance state in electromigrated Ni nanojunctions.[20] In ferromagnetic alignment, the spin-up and spin-down electrons contribute to the conductance in different ways at the domain wall, while in antiferromagnetic alignment the contribution to the conductance from spin-up and spin-down electrons is the same. The antiferromagnetic alignment is considered in the absence of a magnetic field. Thus, to remove the domain wall at the constriction, we forced the magnetization of the two Ni electrodes to be aligned in the same direction by applying a magnetic field of 250 Oe, which is larger than the coercive force, in parallel with the Ni wire during stretching from $\sim$10 000G_0 to the atomic-scale contact. Here two current coils wound outside the Ni wire are set at both sides of the constriction.[21] The histogram in the magnetic field is modified from that in the zero field, likely due to the formation of ferromagnetic alignment of the Ni wires, as shown in Fig. 1. It is significant that a Fano resonance with a zero-bias anomaly is seen during the stretching, as in the case of zero field, as shown in Fig. 2(b). From these results, the electron scattering on large scale domain walls is not considered as the origin of the Fano resonance. On the other hand, we comment that the presence of ferromagnetic domains on the smaller length scales cannot be ruled out by this procedure because a larger field is needed to remove them.

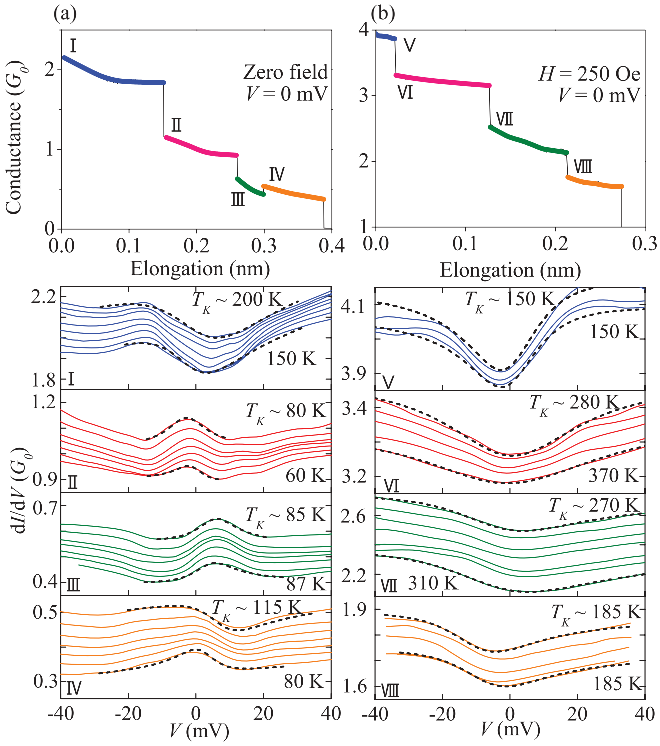

FIG. 2. (Color online) (a) The conductance (upper panel) and the differential conductance dI/dV (lower panel) in the final stage of breaking, which are measured simultaneously. The four lower panels show the evolution of dI/dV for the regions I, II, III, and IV in the conductance. (b) Effect of magnetic field of $H = 250$ Oe on the differential conductance where the magnetic field is applied in parallel with the Ni wire during the stretching. The lower panels show the evolution for the regions V, VI, VII, and VIII in the conductance. The dotted lines are fits by Eq. (1).

As shown in Figs. 2(a) and 2(b), the Fano resonance curve is confirmed in atomic-scale contacts prepared from a Ni wire. Next, we investigate the contact size dependence of the Fano resonance spectra to explore the origin of the zero-bias anomaly. Figure 3 shows representative spectra of dI/dV from $G(0) \sim 1.8G_0$ to $\sim$85G_0, where the size of the constriction with $1.8G_0$ is nearly atomic scale. It is surprising that the zero-bias anomaly is clearly seen up to $G(0) \sim 85G_0$. Assuming that the value of the conductance jump due to the removal of a single atom is about $1.7G_0$, the contact size of $85G_0$ is roughly estimated to be a 50-atom configuration. The magnitude of the anomaly is nearly constant above $G(0) \sim 10G_0$ as plotted in Figs. 3(d)–3(f), while the ratio of the depth of the anomaly to $G(0)$ is suppressed. Consequently, the dI/dV spectra approaches the ohmic behavior in the bulk, with increasing $G(0)$. Moreover, in addition to the zero-bias anomaly a hump grows rapidly for $V \leqslant |25|$ mV above $10G_0$, which is a characteristic seen in large size constrictions with the inelastic scattering between the conduction electrons

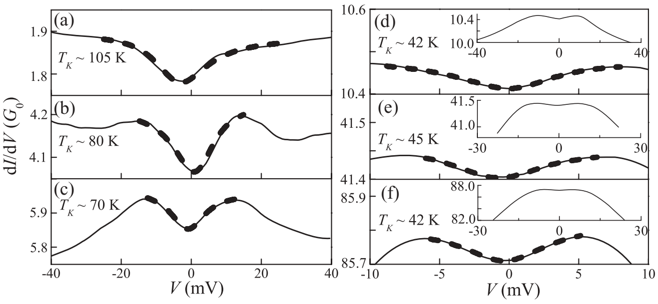

FIG. 3. Representative spectra of dI/dV from $G(0) \sim 1.8G_0$ to $\sim 85G_0$, where $G(0)$ increases from (a) to (f). The dI/dV spectra in (d), (e), and (f) enlarge the zero-bias anomaly, while the insets show the whole image. All spectra exhibit the Fano resonance with the anomaly at around zero bias, which can be fitted by the Fano line shape in Eq. (1).

and phonons.[22,23] These features above $10G_0$ imply that the electronic properties approach those in the bulk, which is consistent with the theoretical calculation that the spin polarization above $5G_0$ is almost identical to the bulk.[13] It is noted that the hysteresis loop due to the itinerant ferromagnetism is shown in Ni nanoparticles with diameters of a few nanometers.[24]

We plot T_K distribution as a function of the contact size $G(0)$ in Fig. 4(a). T_K changes enormously with $G(0)$. In the region of a single atom contact, it is approximately $T_K = 100\text{ K} \pm 50\text{ K}$. As $G(0)$ increases, it decreases gradually. Finally, it seems to be almost a constant at $T_K \sim 40$ K above $15G_0$. In the Kondo model, T_K is given by

$$k_B T_K = W \exp\left[-\frac{1}{J_{cd} D(E_F)}\right], \qquad (2)$$

where W is the bandwidth, J_{cd} is the interaction between the conduction electrons and d electrons, and $D(E_F)$ is the local density of states at the Fermi energy E_F. J_{cd} and $D(E_F)$ are governed by the local properties of the constrictions, which show normal distributions. We plot the histograms of T_K below $15G_0$ and above $15G_0$ in Fig. 4(b), which follow the log-normal distributions of T_K with different mean values. In addition, the temperature dependence of the amplitude for the Fano resonance can be fitted by a logarithmic function as shown in Fig. 4(c), although the temperature range is limited for $1.9 \leqslant T \leqslant 15$ K. Accordingly, it is reasonably considered that the Fano resonance is caused by the Kondo effect not only in the atomic scale contacts as reported by Calvo *et al.*,[11] but also above $15G_0$ at the present situation. The fact that T_K is almost constant and the distribution above $15G_0$ is suppressed compared to that below $15G_0$ may be further evidence that the local properties in the constriction are close to the bulk property.

The results suggest that the Kondo resonance is retained in ferromagnetic Ni constrictions exhibiting bulk properties. In other words, the Kondo effect and ferromagnetism may coexist in the constrictions. According to Calvo *et al.*,[11] when a ferromagnetic wire is reduced to the size of a single atom, the ferromagnetic interaction between d electrons is decreased, whereas the antiferromagnetic interaction between d electrons and sp conduction electrons is increased due to

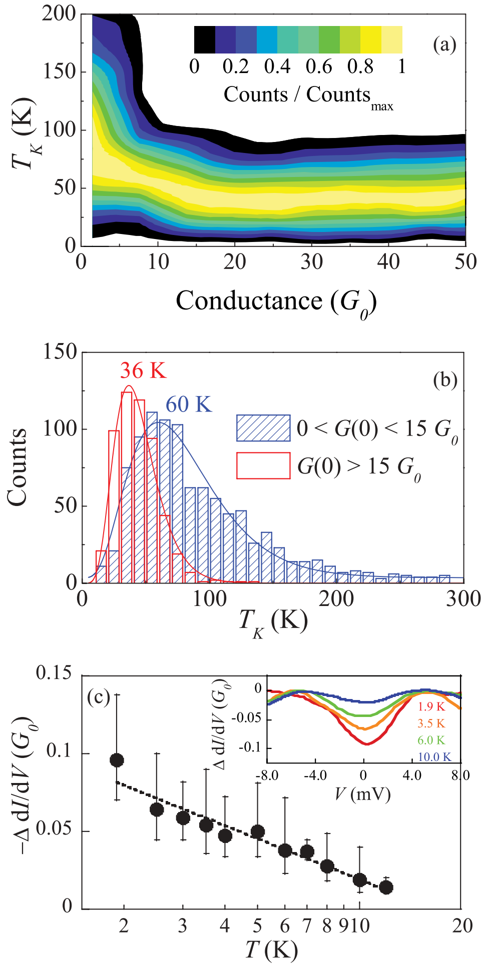

FIG. 4. (Color online) (a) $G(0)$ dependence of T_K distribution, which is estimated at 14 different $G(0)$ values from fitting dozens of the conductance curves for each $G(0)$. To look at the distribution clearly, the distribution is plotted in ten steps, where the counts summed in 10 K steps of T_K are divided by the maximum counts for the step at each $G(0)$. (b) Histogram of T_K below $15G_0$ and above $15G_0$. The continuous line shows the fit of the data to the log-normal distributions of T_K, where most frequent values are $T_K = 60$ K below $15G_0$ and $T_K = 36$ K above $15G_0$. (c) The temperature dependence of the amplitude for the zero-bias anomaly, which is obtained by dozens of the conductance curves between $30G_0$ and $40G_0$ at each temperature. The continuous lines in the inset show the representative curves at 1.9, 3.5, 6.0, and 10 K.

the smaller number of neighboring atoms. As a result, the conduction electrons efficiently screen the magnetic moments of the atomic contacts. However, the present results, observed even in the bulk, are clearly inconsistent with this explanation.

What is the origin of the Kondo effect in the constrictions? Figure 2 represents that the spacial geometry of the Ni constriction plays a crucial role for the variation of the Kondo resonance spectra, suggesting that the geometry is key to the appearance of the Kondo effect. Generally, the Ni constriction has a nonuniform structure in the stretching process by MCBJ.[13] To simplify the analysis on the constriction, we assume a bridgelike structure where a Ni atom is placed on the Ni chain or surface like a bridge. Our theoretical calculation shows that the magnetic moment of the bridge atom is increased from the bulk value due to the formation of an anisotropic structure in the crystal environment.[25] Thus, a bridgelike atom forms a localized level, bringing about the antiferromagnetic Kondo coupling J_{cd}^{AF} due to the hybridization with the conduction electrons. The size dependence of T_K in Fig. 4(a) can be explained by variation of J_{cd}^{AF} and the density of states at Fermi energy $D(E_F)$ in Eq. (2). At large size constrictions, J_{cd}^{AF} and $D(E_F)$ are less affected by the contact size, making T_K almost constant above $15G_0$. In smaller contacts, on the other hand, $D(E_F)$ increases drastically with decreasing the contact size, resulting in the enhancement of T_K.

The importance of the spatial geometry for the conductance has been pointed out by Tossati *et al.*, in a study of Au-Ni-Au chains, which describes the origin of a Fano resonance.[26,27] According to their study, in the bridge geometry of a Ni impurity placed on the Au chain, the conduction electrons traveling in the leads scatter differently in the Ni impurity with two symmetry channels, even and odd. The former is related to the Ni 4s orbital with spin moment $S \sim 0$, whereas the latter is related to the Ni 3d orbital with $S \sim 1/2$ giving rise to the Kondo effect. The interference of the electrons between the two channels causes a Fano resonance. The situation where a Ni atom is embedded on the Ni chain is qualitatively similar to that in the Au-Ni-Au chain from the viewpoint of the formation of an anisotropic structure, implying that the Fano resonance appears in the only Ni chain. The evolution of the differential conductance can be understood more explicitly by considering the change of the spatial geometry due to the stretching.

In conclusion, we suggest that the Kondo effect and ferromagnetism could coexist in Ni nanoconstrictions from the contact size dependence of a Fano resonance using MCBJ technique. A Fano resonance with a zero-bias anomaly appears in Ni atomic-scale contacts, and changes shape as the size of the contact changes. Moreover, the zero-bias anomaly persists in large size constrictions exhibiting bulk properties, where the width is almost constant. We suppose that the spacial geometry of the Ni chain plays a crucial role for the appearance of the Kondo resonance.

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[*] kawae@ap.kyushu-u.ac.jp

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