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Superconducting phases of Bi and Ga induced by deposition on a Ni sublayer

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Thin films of Bi and Ga deposited at 300 K on thin Ni underlayers are strongly coupled superconductors at liquid-helium temperature. A layer of 0.1–5.0 nm of Ni apparently seeds a superconducting phase in each of these metals. For Bi films $T_c \leq 4$ K, with an energy gap $2\Delta \leq 1.30$ meV; for Ga films $T_c \leq 7$ K and $2\Delta \leq 2.30$ meV. For both elements $2\Delta/kT_c \approx 4.2$. The superconductivity of the Bi film *was not* confined to the interface, but extended throughout the film up to thicknesses of at least 40 nm, as was shown by tunneling studies on each surface of the film. X-ray diffraction shows that the Bi films grow pseudomorphically as an fcc phase with the lattice parameter of 5.71 Å, in contrast to the orthorhombic structure of bulk Bi. Upper critical fields were measured as a function of temperature and were several teslas. Ga films with or without seeding with Ni show only a disordered structure by x-ray diffraction. Electron-spin-polarization tunneling studies indicate that the Ni underlayers up to a thickness of about 2.0 nm are not ferromagnetic.

I. INTRODUCTION

The semimetal Bi is an example of those elements that do not display superconductivity under ordinary circumstances, but undergo superconducting phase transitions upon being subjected to hydrostatic pressure or when in the amorphous state. Above ~25 kbars of pressure, Bi shows superconductivity within a T_c ranging from 3.9 to 8.6 K.[1] Bi films form an amorphous phase when quench condensed onto liquid-helium-cooled substrates and have a T_c of 6.2 K.[2] Ga, on the other hand, has a T_c of 1.08 K in the bulk form and under pressure it rises to 6–7 K.[1] Supercooled phases of Ga have been reported to have T_c ranging from 6.2 to 7.8 K.[2-4] Quench condensed on liquid-helium-cooled substrates, amorphous Ga films have a T_c as high as 8.6 K.[2] Amorphous films of both Bi and Ga are strongly coupled superconductors with the reduced BCS parameter $2\Delta/kT_c > 4.2$.[2,3]

In contrast to the above studies, in this work we report superconductivity in films of Bi and Ga grown on room-temperature and liquid-nitrogen-cooled substrates by initially seeding the substrate with an ultrathin film of Ni, which is a ferromagnetic metal. Alloys of Bi with Ni, viz., Bi_3Ni and BiNi, are known superconductors.[5] However, the results described here clearly show that the effect in Bi depends not on alloy formation, but rather the formation of a different crystal structure. In the case of Ga it is unclear at present if it forms a supercooled structure (such as β or γ phase)[2-4] or another phase.

II. EXPERIMENTAL

Bi and Ga films were vacuum evaporated onto liquid-nitrogen-cooled or room-temperature glass substrates in a pressure of $\sim 10^{-7}$ Torr (pumped by diffusion pump, Ti sublimator and cold trap). Initially, a thin layer of Ni was deposited on the substrate, followed by either Bi or Ga. The films were then warmed to room temperature and exposed to the atmosphere before cooling down to low temperatures. The Ni thickness was varied from 1 to 50 Å. The film thickness range for Bi and Ga was from 80 to 1500 Å and 60 to 1000 Å, respectively. In order to make tunnel junctions, a 42 Å thick Al strip was first deposited on a cooled substrate, and at room temperature the top surface was oxidized with a glow discharge to form an Al_2O_3 tunnel barrier. Ni/Bi or Ni/Ga cross strips were then deposited over this Al strip, thus yielding $Al/Al_2O_3/X$ (X=Ni/Bi or Ni/Ga) junctions. To study the Bi side of Ni/Bi, first Ni/Bi was deposited and either the top surface was glow discharged in O_2 to form BiO_x, or a thin layer of amorphous Si was deposited to form the tunnel barrier. Al or Ag long strips over this resulted in either Ni/Bi/Si/Al or Ni/Bi/BiO_x/Ag tunnel junctions. (Artificial Al_2O_3 barriers on Ni/Bi were also tried but successful junctions had resistance >1 MΩ.) Films of Bi were also made over other elements, such as Pt, Cu, Fe, Si, and Cr in the place of Ni, as the nucleation layer. Tunnel junctions of the kind Al/Al_2O_3/Bi were used to study orthorhombic Bi band structure.

III. RESULTS

A. Ni/Bi films

In the following we refer to the thickness of Ni and Bi used as n/m, where n and m are the Ni and Bi thicknesses (in Å), respectively. For example, 4/800 Ni/Bi stands for 4 Å of Ni below 800 Å of Bi. (The same notation is used for Ni/Ga films in the next subsection.) Ni/Bi films had high resistivity; thicker films showed metallic behavior as the temperature was lowered from room temperature to 4.2 K, whereas the resistance of thinner Ni/Bi films was nearly independent of temperature. For instance, 10/400 Ni/Bi film had a resistivity of 1000 $\mu\Omega$ cm before it went superconducting at 3.8 K. On the other hand, pure Bi films always showed an increase in resistivity upon cooling.

The transition temperature of Ni/Bi films ranged from < 1 to 4 K. For Ni films 1 to 1.5 Å thick, T_c ranged from < 1 to 2 K; for 4 to 50 Å of Ni, sharper transitions occurred with T_c between 3.3 and 4 K. For thinner Bi films (< 160 Å) with 50 Å of Ni below, T_c dropped to < 1 K as was also the case for a very thin Ni nucleating layer, whereas 50/800 film had a T_c of 3.8±0.1 K. With Pt, Cu, Fe, Si, or Cr as the nucleation layer, Bi did not show any sign of superconductivity down to 0.9 K. Also, Bi films 140 Å thick with 4 Å of Ni over them were not superconducting down to 1 K. Co-evaporating Ni and Bi to give Bi_3Ni and BiNi films about 100 Å thick on cooled substrates and subsequently warming to room temperature, with no additional annealing, produced nonsuperconducting samples, even down to about 0.9 K.

Superconducting tunneling characteristics were measured for several junctions of the kind $Al/Al_2O_3/Ni/Bi$ in the low bias voltage range. Two examples of tunneling conductance curves showing superconducting energy gaps are displayed in Fig. 1 for 4/800 and 10/85 NiBi films. These Ni/Bi films had transition temperatures of 2.4 and 3.6 K, respectively. In Fig. 1(a) only the peaks at the sum of the gaps are seen, whereas in Fig. 1(b) peaks are observed at both the difference and sum of the gaps. From these data $2\Delta_{AL}=0.72$ meV and $2\Delta/kT_c=3.5$, which agrees well with our earlier studies. The energy gaps obtained for Ni/Bi are 1.23 and 1.30 meV, respectively, for 4/800 and 10/85 samples. The onset of superconducting energy gaps was used to check the T_c in a few cases and showed good agreement with the resistive T_c. These data lead to $2\Delta/kT_c$ of 4.3 to 4.4, respectively, for these Ni/Bi samples. Many tunnel junctions were studied and all showed similar values. Those Bi junctions without Ni showed only an Al energy gap.

Tunnel junctions were made in the reverse order to explore the superconducting behavior of the top surface of Bi, i.e., the side away from the Ni/Bi interface. For instance, Ni/Bi/Si/Al junctions (with amorphous Si barriers) showed a superconducting energy gap for the Bi surface. However, peaks in the conductance curves were broad, making it difficult to deduce an accurate value of the energy gap. This is typical of Si or Ge artificial barriers.[6] On the other hand, $Ni/Bi/BiO_x/Ag$ junctions showed well-defined conductance peaks in the tunneling curves (Fig. 2) from which the superconducting energy gap for Ni/Bi (4/400) is estimated as 0.92 meV. The resistive transition of this film was about 2.5 K and somewhat broad, which could perhaps be caused by the effect of the glow discharge on Bi. A value of $2\Delta/kT_c \geq 4$ was obtained for this film.

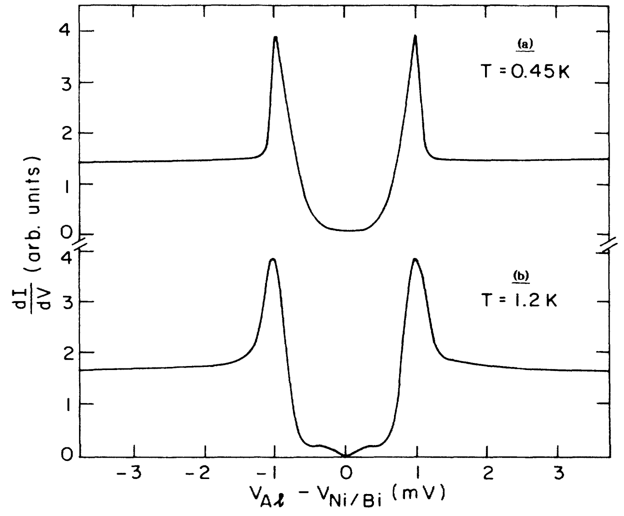

FIG. 1. Tunnel conductance plotted as a function of applied bias for two $Al/Al_2O_3/Ni/Bi$ tunnel junctions with Ni/Bi of 4/800 (a) and 10/85 (b) showing superconductivity at the Ni/Bi and Al with the Al_2O_3.

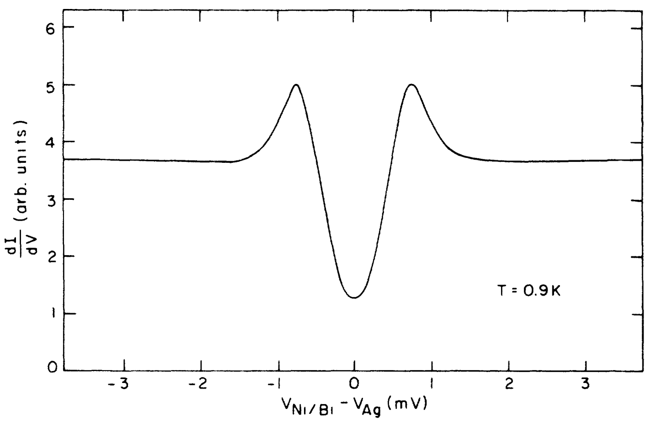

FIG. 2. Tunnel conductance curve for $Ni/Bi/BiO_x/Ag$ tunnel junction vs applied bias showing superconducting energy gap on the top surface of Bi for Ni/Bi of 4/400.

To investigate the energy band structure in Bi, tunnel conductances were measured at higher voltages for samples made under several conditions. Bi band structure was not observed even at 1.2 K in Ni/Bi tunnel junctions from above the superconducting gap structure to 1.5 V.

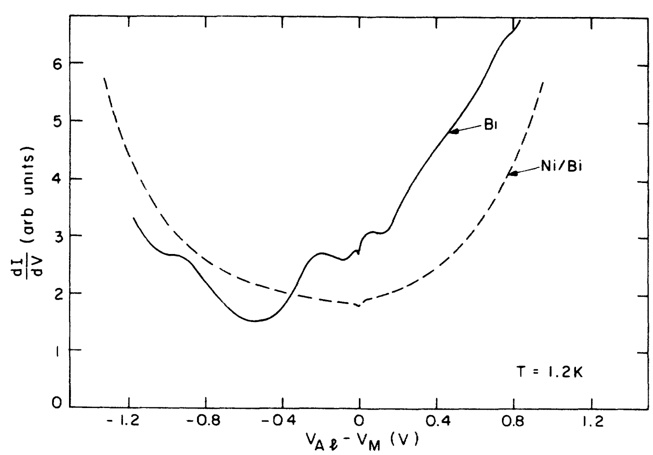

FIG. 3. Higher bias range conductance curves showing Bi band structure for the orthorhombic phase (ordinary phase) of Bi and the absence of band structure in Ni/Bi film. In both cases, oxidized Al was the counter electrode.

This was the case for *both* surfaces of Bi. Instead, structureless, nearly parabolic dependence of conductance as a function of applied bias, was observed. In contrast, junctions without Ni displayed Bi band structure. These are shown in Fig. 3. The conductance peak positions for Bi junctions agree well with those observed earlier by Hauser and Testardi[7] for Bi films. Except in the case of thinner Pt (<4 Å), tunnel junctions with other elements used as nucleation layers did not show Bi band structure. For Pt/Bi films (with <4 Å Pt), less resolved structures of Bi bands were observed, somewhat displaced in position compared to the pure Bi case.

Irrespective of Bi thickness, Ni/Bi films showed substantial critical fields (H_{c2}). For example, 4/140 and 4/800 films showed H_{c2} of 3 to 9 T. H_{c2} plotted versus temperature is shown in Fig. 4 for a 4/140 Ni/Bi film with the applied magnetic field in the plane and perpendicular to the plane of the film. Anisotropy in H_{c2} is well exhibited with $H_{c2}^{\parallel}(0)$ being three times higher than $H_{c2}^{\perp}(0)$. The initial slopes, $dH_{c2}^{\parallel}/dT$ and $dH_{c2}^{\perp}/dT$, at T_c are 6 and 2 T/deg, respectively. The coherence length evaluated from $H_{c2}^{\perp}(0)$ is 97 Å for this film, with values for other films being not significantly different.

The crystal structure of these films was studied by powder x-ray diffraction with Cu$K\alpha$ radiation at room temperature. A sample for x-ray study was prepared at 77 K by depositing a 400 Å thick Bi film on a glass slide half covered with 4 Å Ni, and then warming to room temperature. In Fig. 5 the diffraction pattern obtained for a pure Bi film is compared with that of a Ni/Bi film. The major peak positions in the two cases are seen to be very different, indicating different crystal structure for the two samples. The d spacings calculated from this for Bi are 3.96, 1.98, and 1.323 Å with intensity ratios of 100, 80, and 7, respectively. Corresponding values for Ni/Bi are 3.29 and 1.65 Å with relative intensity ratios of 100 and 5, respectively. There are no reported peaks for pure Bi at these two positions. One can also see a few more very weak peaks in Ni/Bi whose intensities are $\sim 1\%$, two of which seem to correspond reasonably with the pure Bi pattern. Bulk Bi has rhombohedral crystal structure. If one assumes that the crystal structure of Ni/Bi is fcc, which is reasonable since Ni has an fcc structure, then the peak at $d=3.29$ Å is (111) and (222) peak occurring at $d=1.65$ Å. The average lattice parameter obtained self-consistently from these two peaks is 5.71 Å, which may be compared with equivalent hexagonal cell parameters for bulk Bi of $a=4.536$ Å and $c=11.836$ Å. X-ray data thus indicate that Bi grows pseudomorphically in fcc structure when deposited over Ni with a preferred (111) orientation.

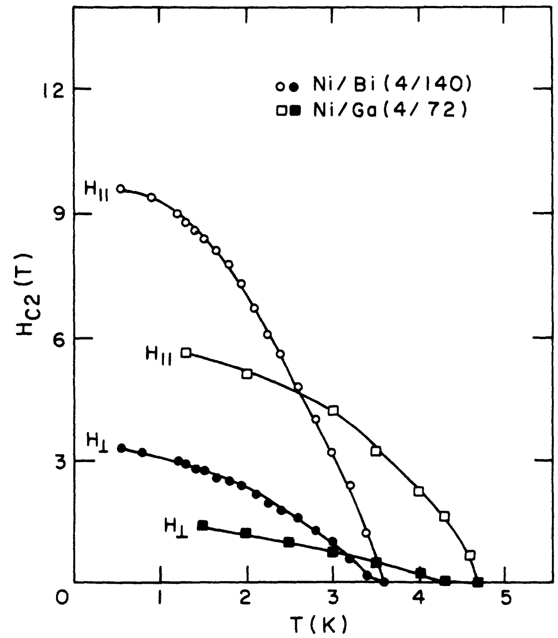

FIG. 4. Upper critical field (H_{c2}) as a function of temperature in thin films of Ni/Bi and Ni/Ga with the applied magnetic field parallel ($H_{\parallel}$) and perpendicular ($H_{\perp}$) to the film plane.

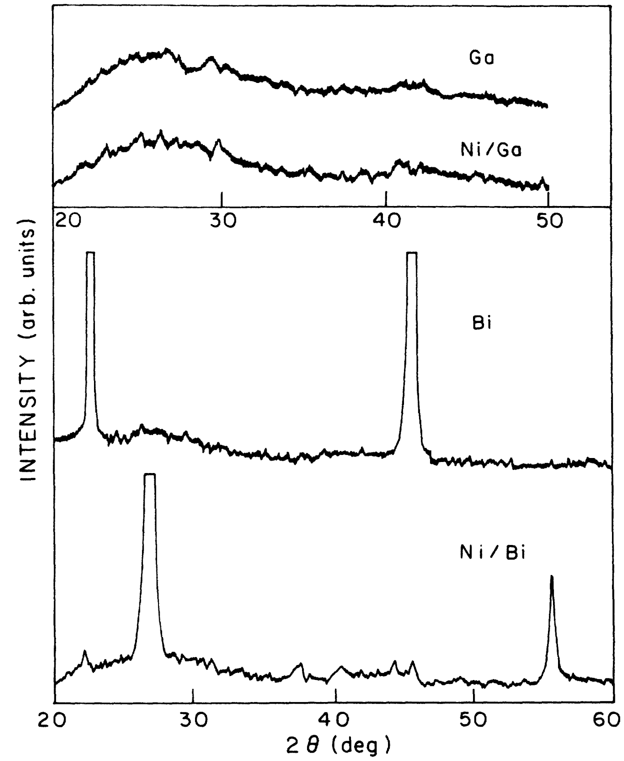

FIG. 5. X-ray diffraction pattern at room temperature with Cu$K\alpha$ radiation for Bi, Ni/Bi, Ga, and Ni/Ga films.

B. Ni/Ga films

These films were prepared in the same manner as Ni/Bi films. Tunnel junctions were made on Al films oxidized in a glow discharge. Ni/Ga films showed *metallic behavior* in film resistance as a function of temperature upon cooling, saturating below about 20 K before becoming superconducting by 5–7 K. As the thickness of Ga was lowered (thinner samples were protected by a 50–100 Å thick film of Al_2O_3), the drop in resistance decreased, but remained metallic. For thinner, unprotected films, although most of the resistance was lost by 4.2 K, a small tail remained until about 3.3 K. Film resistivities just above T_c were in the range 25–60 $\mu\Omega$ cm. Thicker films had lower resistivity—e.g., a 20/1000 film had a resistivity of 25 $\mu\Omega$ cm and residual resistivity ratio of 2.5. The films were stable at room temperature. They were stored in a desiccator before cooling down. Thicker films were stable for >2 years, retaining nearly the same T_c, whereas thin films became discontinuous in a few days, especially without the protective Al_2O_3 coating.

Tunneling conductances were measured for several junctions of the type $Al/Al_2O_3/Ni/Ga$. Shown in Fig. 6 are two such curves for 4.8/240 and 20/1000 Ni/Ga taken at 1.2 K and 1.35 K, respectively. The 42 Å Al counter electrode had a T_c of 2.4 K. Peaks at the difference and sum gap voltages are distinctly seen. The superconducting energy gap for the two Ni/Ga films were found to be 1.85 and 1.13 meV, the higher gap value being that of thinner films. In a few cases the onset of the superconducting energy gap was also used to identify the T_c of the films, with good agreement with the resistively determined T_c. The value for $2\Delta/kT_c$ ranged between 4.2 and 4.5, indicating strong-coupling superconductivity in Ni/Ga films. Tunnel junctions were also made successfully by layering Ni and Ga (5 and 100 Å thick, respectively, repeated four times) on an oxidized Al counter electrode, yielding a 2Δ of 1.82 meV.

Tunnel conductance at higher bias was measured in a few cases, showing a parabolic dependence of conductance versus voltage. Attempts to make junctions in the reverse order, i.e., putting down an artificial barrier over Ni/Ga to look at the superconducting behavior of the surface of Ga, were not successful. Glow discharge in O_2 was not attempted on these thin Ga films to avoid heating.

Critical magnetic field measurements were performed as a function of temperature for Ni/Ga films. Thick films (e.g., 20/1000) showed H_{c2} values of only a few kOe, whereas, as seen in Fig. 4, thinner films had H_{c2} of several tesla. The anisotropy ratio $H_{c2}^{\parallel}/H_{c2}^{\perp}$ is about 4 at low temperatures for this 4/72 sample. The initial slope of $H_{c2}^{\perp}$ is 0.49 T/K and a coherence length of 146 Å is deduced from the extrapolated $H_{c2}^{\perp}(0)$ for this Ni/Ga film.

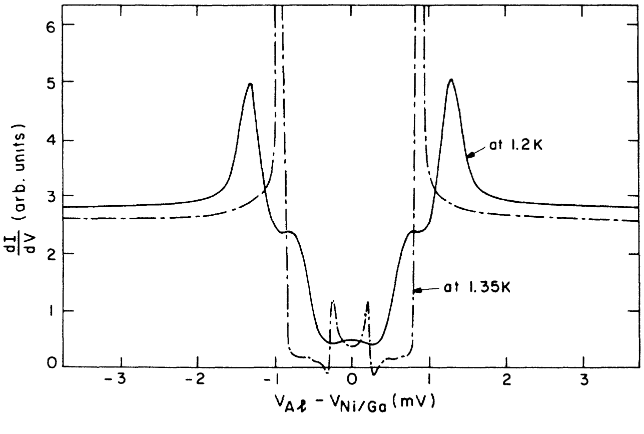

FIG. 6. Tunnel conductance vs applied bias for $Al/Al_2O_3/Ni/Ga$ junctions for 20/1000 (— - — - —) and 4.8/240 (——) Ni/Ga films showing the superconducting sum and difference peaks in these films.

The present $H_{c2}^{\perp}$ data are similar to the data for thick amorphous Ga films measured by Bergmann.[8]

X-ray studies were done for the Ni/Ga films to determine the crystal structure. A cooled glass substrate was half covered with 4 Å of Ni and then 400 Å of Ga was deposited over the whole substrate. After warming to room temperature, x-ray diffraction patterns were taken for both pure Ga and Ni/Ga, as shown in Fig. 5. Only a broad background is observed for both films showing disordered structure.

IV. DISCUSSION

Amorphous Bi and Ga films formed when deposited on liquid-helium-cooled substrates have T_c's of 6.2 and 8.5 K, respectively.[1–4] But upon warming up to room temperature (or even ~100 K), the superconducting phase is destroyed in Bi films, whereas in Ga films T_c drops to ~2–3 K.[2,3] When Ga is evaporated onto a room-temperature substrate in the presence of O_2, superconductivity has been observed, which has been attributed to β, γ, and δ phases of Ga.[3] Our present results, which were obtained for films deposited at near 77 or 300 K with Ni as the nucleating layer, and then stored at 300 K before cooling down to liquid-helium temperatures, show clearly the necessity for the Ni layer. Without the presence of Ni film, no superconductivity was observed. Ni/Bi films are not amorphous but have fcc crystal structure of nearly (111) orientation. Ni/Ga films do not unequivocally exhibit evidence of being amorphous or crystalline at room temperature. Alloy formation (viz., Bi_3Ni or BiNi)[5] in these samples is ruled out because when Ni was deposited over Bi, superconductivity was not seen. Also, it is not just an interface effect in Ni/Bi since we see a superconducting energy gap on both sides of the Bi films in 4/400 Ni/Bi, confirming the absence of alloy formation. Furthermore, Bi_3Ni or BiNi compounds have noncubic crystal structure, whereas our Ni/Bi films have cubic structure. The absence of Bi band structure and the formation of the fcc phase of Bi may indicate that the density of states at the Fermi level is increased in these Bi films, thereby causing superconductivity. The same argument perhaps applies to Ga films as well.

Another interesting observation is that even with 50 Å of Ni below the Bi (which was 800 Å thick), superconductivity was clearly seen. In our previous studies[9,10] on the magnetic behavior of Ni films, 50 Å of Ni was ferromagnetic when in contact with Al, Au, Pb, etc. When in contact with Al, Ni needed to be three monolayers thick to be ferromagnetic. In a series of recent experiments we have studied[10] the magnetic behavior of isolated atoms, submonolayers, and monolayers of Ni quench condensed on various metal film substrates by *in situ* magnetic inductance measurements at 4.2 K in UHV conditions. Although the magnetic moment of Ni was reduced over Al, Pb, Sn, etc., it was finite even at the lowest coverages (< 1 Å); on Au, Cu, or Ag surfaces, there was no significant reduction in the Ni moment. The above studies also were conducted on freshly quenched-condensed superconducting Bi films. Ni deposited over this, *in situ*, showed depairing of Cooper pairs in Bi, similar to that on Pb surfaces, showing a finite magnetic moment in Ni even for submonolayer coverage.

Although superconductivity was observed by the drop in resistivity for Ni/Bi with 50 Å Ni and Bi films of 150–800 Å thickness range, a superconducting energy gap was not observed on the Ni side of 50/800 samples (with a T_c of 3.8 K). Also, thinner Bi films with a thick Ni layer (e.g., 50/168 film) did not completely lose its resistance by 1 K, whereas 50/192 or 10/85 films showed complete superconductivity. These results imply that the thicker Ni films retain their ferromagnetism at least partially and depair the adjacent superconductor. In the case of 20/1000 Ni/Ga, which showed complete superconductivity (Fig. 6), attempts were made to measure electron-spin polarization on the Ni side of the film. At 0.4 K and in a field of 3.5 T, no significant polarization was seen. This indicates the absence of ferromagnetism in this Ni layer. Similarly, junctions with Ni/Bi did not show any finite polarization in a magnetic field larger than the H_{c2} for the Ni/Bi film.

These data strongly suggest that at least for thicknesses up to 20 Å of Ni, the Ni is not ferromagnetic when covered by either Bi or Ga. This thin layer of Ni is driven into a superconducting state as evidenced by the superconducting energy gap at the Ni surface of Ni/Bi or Ni/Ga. However, for thicker Ni films, no superconducting gap is observed, which indicates the magnetic nature of the Ni films. The picture that emerges from this study is the following. A thin seeding layer of Ni drives the subsequently grown Bi film (very likely Ga, too) into a pseudomorphic fcc structure which turns out to be a superconductor. This superconductor in turn destroys the magnetic interaction in Ni and drives it into a nonmagnetic metal which is superconducting because of the proximity effect of the superconducting Bi, at least for Ni films no thicker than about 20 Å.

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