Effective Exchange Energy in a Thin, Spatially Inhomogeneous CuNi Layer Proximized by Nb

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ABSTRACT: Thin films of diluted magnetic alloys are widely used in superconducting spintronics devices. Most studies rely on transport measurements and assume homogeneous magnetic layers. Here we examine on a local scale the electronic properties of the well-known two-layer superconductor/ferromagnet structure Nb/CuNi. Scanning tunneling spectroscopy experiments demonstrated significant spatial variations of the tunneling conductance on nanoscale, with characteristic gapped, nongapped, and strongly zero-bias peaked spectra. The microscopic theory successfully reproduced the observed spectra and relied them to spatial variations of CuNi film thickness and composition, leading to strong variations of the effective exchange energy. The observed inhomogeneities put constraints on the use of diluted magnetic alloys in nanoscale devices.

The current challenge for modern electronics is to discover new physical principles and explore technological routes for next-generation computing devices. In this trend, superconducting electronics has numerous advantages owed by its energy efficiency (in the attojoule range per operation), high performance (clock speed reaching 100 GHz), and well-established fabrication technologies. In these devices, cryogenic memories, valves, and magnonic metamaterials are based on heterostructures combining superconducting (S) and ferromagnetic (F) materials. There are also many fundamental studies aimed specifically at studying the coexistence of superconductivity and magnetism at the micro scale.

Wide-range applications of superconductor-ferromagnet (SF) hybrids in quantum electronics are often limited by a high exchange energy $E_{\text{ex}}$ and a small superconducting gap in conventional superconductors. As a result, the penetration depth of superconducting correlations into F is extremely short, on the order of nanometers, which implies the use of ultrathin F layers, which is technologically challenging. Furthermore, the characteristic voltage $V_{c}$ (characteristic frequency $\omega_{c}$) of the experimentally investigated SFS heterostructures is on the order of 2 orders of magnitude lower than the $V_{c}$ of SIS Josephson junctions (sandwiching insulating materials I between the two S electrodes) currently used in superconducting logic devices.

With the idea of reducing $E_{\text{ex}}$ and $V_{c}$, several reports proposed to use diluted ferromagnetic alloys, such as CuNi and PdFe, and other dilute magnetic elements like CuNi, PdFe, and CoFe. In the case of CuNi, it enabled one to reduce the effective exchange energy $E_{\text{ex}}$ down to $E_{\text{ex}} = 850 \text{ K}$, as compared to 2000 K in pure Ni. The reduction by a factor of 2 is indeed expected from our calculations provided for Cu$_{90}$Ni$_{10}$ alloy (available in Supporting Information).

Though, the available literature does not provide much information on the degree of spatial inhomogeneity of the used dilute alloys. Without this information, it is difficult to evaluate the perspectives of miniaturization of F-containing superconducting electronics elements, as well as the robustness of their working parameters.

In the present work, we reveal the inhomogeneous character of morphology, electronic, and magnetic properties of vacuum prepared CuNi/Nb bilayers. We combine low-temperature tunneling microscopy and spectroscopy (STM/STS) with magnetic force microscopes and compare the experimental data with the results of calculations in the framework of the microscopic theory of superconductivity.

For STS measurement, CuNi/Nb bilayers were grown by consecutive magnetron sputtering of CuNi and Nb targets onto SiO$_2$ substrate. The studied samples contained 7 ± 1 nm thick CuNi and 100 ± 4 nm thick Nb films. The use of SiO$_2$ substrate enabled avoiding a chemical bonding of CuNi film to the Nb substrate.
substrate. The details of the sample growth are presented in Supporting Information.

STM/STS experiments were provided at temperatures 0.3−2.4 K under ultrahigh vacuum ($P < 1 \times 10^{-10}$ Torr). The technical details are presented in the Supporting Information. A special care was taken in order not to expose CuNi surface to air between the film deposition and tunneling experiment. Indeed, most of STM/STS experiments reported on ex-situ fabricated samples and devices were carried out on surfaces strongly altered and contaminated by exposure to air. To avoid contamination, we used an inverted preparation and in situ cleavage method. The Nb-surface of ex-situ grown samples were glued to the STM sample holder. Then a cleaver was glued on the SiO$_2$ substrate side Figure 1a. The samples were introduced in the STM chamber where they were mechanically cleaved in UHV. Several preliminary cleavage sequences followed by electron microscopy analyses showed that the cleavage always occurs at the interface between CuNi and the SiO$_2$ substrate, which is the weakest interface of the heterostructure. After cleaving, the 7 nm(CuNi)/100 nm(Nb) thick bilayer sample was introduced into the scanning tunneling microscope, Figure 1b.

The results of STM/STS experiments are presented in Figures 1d–f. Figure 1d shows a (300 nm)$^2$ constant-current STM image of the CuNi surface. It presents substantial height variations (3−4 nm), that is about a half of the nominal CuNi film thickness. The simultaneously acquired zero-bias conductance map $dI/dV(V=0,x,y)$ in Figure 1e reveals a spatially inhomogeneous distribution of electronic properties. On this map, the regions in blue present a fully opened proximity mini-gap, $\Delta_{\text{mini}} \approx 0.35$ meV (blue curve in Figure 1f), while the regions in red are characterized by an almost normal density of states (red curve in Figure 1f). Spatially, the signal varies from fully gapped (in blue) to normal (in red) on a scale of a few nanometers. These variations are only weakly correlated to the surface morphology: lower regions in STM topographic image, supposedly representing regions of a thinner CuNi, do not always show a larger mini-gap, and vice versa. A possible explanation for such a behavior is that, in addition to thickness variations, the $x$-content of the Cu$_{1-x}$Ni$_x$ alloy also varies; apparently, there are several characteristic lateral scales of these variations.

Additional magnetic force microscopy (MFM) experiments performed on CuNi films at 4.5 K also revealed spatially varying patterns, Figure 2. The latter could be related to magnetic domains spontaneously formed below Curie temperature, but also to a nonuniform concentration of Ni in CuNi alloy (magnetic properties of the studied CuNi films are further discussed in the Supporting Information). Note that the characteristic scale $\sim 50−300$ nm of contrast variations in MFM maps is close to the scale of the observed spatial variations of electronic properties (Figure 1e). Future works could shed light on the physical origin of this match.

Figure 1. Scanning tunneling spectroscopy experiment. (a) Schematic representation of the in situ cleaving system: the sample is glued sandwiched between the sample holder and cleaver; the sample is cleaved in UHV by applying a mechanical force to the cleaver. (b) STM tip is approached to the in situ cleaved sample surface. (c) Local tunneling spectra are acquired at the surface of a 7 nm thick CuNi layer located on top of a 100 nm thick Nb film. (d) Constant-current STM image of the exposed CuNi surface. Significant height variations are observed. (e) zero-bias conductance map of the same area as in part d. Most of the surface present spatial coexistence of regions characterized by the presence (dark blue) and the absence (red) of the superconducting gap. (f) Typical shapes of $dI/dV(V)$ tunneling spectra acquired in gapped (blue) and nongapped (red) regions in part e.
Figure 2. Magnetic force microscopy map of 70 nm thick CuNi. The map shows spatial variations of the phase of magnetic cantilever oscillations that reveals a domain structure with a typical size of 50–300 nm (a more detailed study of magnetic properties is presented in the Supporting Information, Appendix YYY). The scale bar is 0.5 μm.

We now focus on the analysis of typical local tunneling spectra observed in the experiment; they are presented in Figure 3a and Table 1. The mini-gapped spectra (as that presented by blue curve) and flat ones (red curve) were found to be dominant (~49% of area each). Tunneling spectra of other shapes were also observed (orange and green curves). While their presence at the surface is rare (~1% of area each), they were reproducibly recorded. All the spectra (but the flat one) share three common properties: (1) they present peaks in the energy window of a few meV, relevant to superconductivity; (2) the peaks are symmetric with respect to zero bias, reflecting electron–hole symmetry; (3) the peak amplitudes are very high as compared to tiny signatures observed in spatially averaged spectra.

In Figure 3b, we present the tunneling conductance spectra generated numerically using microscopic theory (see Supporting Information). The blue spectrum was generated considering a SN bilayer with no exchange field in N, that is $E_{ex} = 0$. The spectrum demonstrates a clear mini-gap $\Delta_{\text{mini}} \approx 0.4$ meV that is indeed significantly smaller than the gap $\Delta_{\text{Nb}} = 1.4$ meV of bulk Nb. This is realized by taking the N-layer thickness $d_F = 11$ nm, that is above 7 nm nominal thickness of the studied CuNi film. Other parameters are $\xi_F = 20$ nm, $\rho_F = 0.25\rho_S$, and $\gamma_B = 0.1$ (refer to the Supporting Information for details of numerical calculations). Thus, the presence of mini-gap spectra is only possible if nonferromagnetic clusters are present in the CuNi layer.

The numerically generated spectrum in Figure 3b (green curve) reproduces the experimentally observed double-peaked one in Figure 3a. In these spectra, the larger peaks occur at energies close to the superconducting gap of Nb $\Delta_{\text{Nb}}$, while inner peaks are positioned at lower energies, close to $\Delta_{\text{mini}}$. We assume that the spectrum is the result of cotunneling to two clusters of CuNi with significantly different parameters. Numerically, it was generated taking a weighted sum ($0.6 - 0.4$) of two mini-gap spectra with respective parameters $d_F = 7$ nm, $\xi_F = 20$ nm, $\rho_F = 0.6\rho_S$, $\gamma_B = 0.1$, and $E_{ex} = 0$ and $d_F = 11$ nm, $\xi_F = 20$ nm, $\rho_F = 0.25\rho_S$, $\gamma_B = 0.1$, and $E_{ex} = 0$. Note that in both contributions the exchange energy is zero. (See details in Supporting Information.)

The most intriguing are the spectra manifesting a strong double-peak feature near zero-bias (in orange in Figure 3a). Such odd signatures are in fact typical for the ferromagnetic

![Figure 3](https://doi.org/10.1021/acs.jpclett.2c00978)

Figure 3. Analysis of the tunneling spectra. (a) Gapped $dI/dV(U)$ spectra (in blue) are characterized by a mini-gap $\Delta_{\text{mini}} \approx 0.35$ meV (which is about 4 times smaller than the superconducting gap of Nb $\Delta_{\text{Nb}} \approx 1.4$ meV). Along with nongapped spectra (in red), they are dominant on CuNi surface. Red and blue spectra are observed with roughly the same frequency (~49% of area each). Other spectral shapes were occasionally recorded (~1% of area each); Spectrum in orange shows asymmetric double peak around zero-bias (fwhm = 0.44 meV); Green spectrum exhibits a smaller gap $\delta \approx 0.4$ meV within a larger one ($\Delta \approx 1.2$ meV), comparable with $\Delta_{\text{Nb}}$. (b) Tunneling conductance $dI/dV(U)$ spectra calculated for different exchange energies $E_{ex}$ and coherence lengths $\xi_F$ (curve numbers correspond to those in Table 1). The chosen parameters are $d_F = 11$ nm, $\xi_F = 20$ nm, $\rho_F = 0.25\rho_S$, $\gamma_B = 0.1$, and $E_{ex} = 0$ for the “SN”-curve (blue line) and $d_F = 7$ nm, $\xi_F = 20$ nm, $\rho_F = 0.85\rho_S$, $\gamma_B = 3$, and $E_{ex} = 4T_c$ for the “SF”-curve (orange line). The green line is the result of the superposition of two SN-clusters with $E_{ex} = 0$ and $d_F = 7$ and 11 nm, respectively, taken into account with weights 0.4 and 0.6.

Table 1. Parameters of Fits Presented in Figure 3b

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<th>curve number</th>
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<th>$\xi_F$, nm</th>
<th>$\rho_F \mu\Omega$ cm</th>
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<td>100T_c</td>
<td>35</td>
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</tbody>
</table>

From left to right: curve number, F-layer thickness $d_F$, exchange energy $E_{ex}$ normalized to $T_c$, coherence length $\xi_F$ and resistivity $\rho_F$ of F-layers, SF-interface parameter $\gamma_B$. In all fits, Nb- layer parameters were kept fixed: thickness $d_F = 100$ nm, coherence length $\xi_S = 10$ nm, and resistivity $\rho_S = 15.2 \mu\Omega$ cm.
hybrid structures with small exchange energies $E_{ex} \sim \Delta$. For instance, considering a SF-bilayer with the exchange energy $E_{ex} = 4T_c$ results in a spectrum presented in Figure 3b (orange curve). This spectrum demonstrates all the main features of the experimentally observed one. In particular, the splitting of the main peak due to Zeeman effect appears in the structures with homogeneous magnetization, while in systems with inhomogeneous magnetization the zero-energy peak is usually sharp and narrow.

It becomes clear that the understanding of the experimental data requires considering spatial inhomogeneities of the CuNi layer thickness and composition. The system thus consists of regions of different thickness and strongly varying exchange energies. The gapless regions (red regions and red spectrum in Figure 1e,f) are locations where the exchange energy is extremely high, $E_{ex} \gg \Delta$. They coexist with nonmagnetic regions characterized by a fully developed mini-gap. In-between, regions with the exchange energy of the order of the gap $E_{ex} \sim \Delta$ show split peaks at zero-bias. All points toward significant fluctuations of the Ni-content in the layer, which can affect not only the exchange energy locally but also the resistivity and the effective coherence length.

The nonuniformity of ferromagnetic layers can lead to a number of important consequences. For example, $\phi$ junctions can be obtained in Josephson junctions with an inhomogeneous ferromagnetic layer. Structures consisting of two superconducting electrodes separated by a layer of ferromagnetic film with a spatially inhomogeneous exchange energy $E_{ex}$ represent themselves as a parallel connection of spatially localized $0$- and $\pi$-Josephson junctions. In areas with $E_{ex}$ close to zero there are 0-junctions, while in the places with a finite $E_{ex}$ there is a probability for $\pi$-junctions nucleation. Simultaneous existence of these channels are not energetically favorable due to generation of spontaneous supercurrents closed by these channels. In Refs. 46,48–50 it was proved that if the net energy of all 0-channels, $E_0 = \sum_k E_{0,k} \delta_{k,0}$ sufficiently exceeds the net energy of $\pi$-channels, $E_{\pi} = \sum_k E_{\pi,k}$, then the main energy favorable state of the entire structure is the 0-junction, in which all $\pi$-channels are in the energetically nonequilibrium 0-state. In the equilibrium state, the phase difference across a junction $\phi = \phi_{eq} = 0$. These are so-called 0-junctions. Here $\phi$ is phase difference across the junction, $A_{\phi,0}$, $A_{\phi,\pi}$ and $J_{I,0}$, $J_{I,\pi}$ are magnitudes of the areas and the local critical current densities of 0- and $\pi$-channels, respectively.

In the opposite case, $E_{\pi} > E_0$, the SFS junctions is in $\pi$-state, while all 0-channels are in the energetically nonequilibrium $\pi$-state. In the equilibrium state, the phase difference across a junction $\phi = \phi_{eq} = \pi$. These are so-called $\pi$-junctions. In a vicinity of equal energies, $E_{\pi} \approx E_0$, the equilibrium difference $\phi_{eq}$ is determined from the properties of the second harmonic amplitude in the current-phase relation of the SFS-junction. The $\phi_{eq}$ can take any value inside the interval $0 \leq \phi_{eq} \leq \pi$. These types of Josephson junctions were called $\phi$-junctions.

For comparison, in the homogeneous SFS-junction the other $0 + \pi$ state appears in the region of the $0+\pi$ transition with bistable ground states at $\phi_{eq} = 0$ and $\phi_{eq} = \pi$. The other manifestation of the presence of parallel 0- and $\pi$-areas in the structure is the field dependence of the critical current of the junction.52,53

Therefore, the present study sheds light on the origin of the $\phi$-state observed in the vicinity of the $0 + \pi$ transition in planar SFS systems with no intentionally created inhomogeneities.54–58 In those structures, CuNi layers could present copper-rich and nickel-rich clusters providing an intrinsically inhomogeneous N–F network and enabling effective $\phi$ – contacts. The results of previous tunneling experiments32 can also be better understood. Here again, the space-averaging over a strongly $E_{ex}$-varying system would result in the washed out amplitude of spectral signatures while preserving their characteristic energy scales ($\Delta$, $\Delta_{\text{mini}}$, etc.).

We would also underline the importance of the experimental evidence of a decrease in the effective exchange energy observed in certain areas of the CuNi alloy. This is probably explained by the fact that the real trajectories of individual electrons can take place in both the F- and N-regions.59–61 The mechanism of reducing the effective value of the exchange energy is extremely important for the implementation of magnetic Josephson structures for digital devices with high characteristic frequencies.62–65

### ASSOCIATED CONTENT

![Supporting Information](https://pubs.acs.org/doi/10.1021/acs.jpcl.2c00978)

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.2c00978.

Sample preparation, additional experimental details, magnetic properties of CuNi films and description of Usadel model, and Figure S1, sample preparation; Figures S2 and S3, magnetic properties of CuNi films; and Figures S4–S6, tunneling conductance spectra and DOS calculated at CuNi surface for different values of the parameters (PDF).

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Author Contributions

V.S. and D.R. conceived the project and supervised the experiments, V.O. and V.S. performed magnetron thin films deposition, V.S. and T.C. performed the STM/STS measurements, V.S., M.K., A.G., I.S., and D.R. provided the explanation of the observed effects, A.N., S.B., and N.K. constructed the model, A.N. did numerical modeling, V.S. and D.K. performed the MFM measurements and experimental data processing, V.S., N.K., and D.R. wrote the manuscript with the contributions from other authors. All authors have read and agreed to the published version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

MFM experiments were supported by RSF Grant No. 18-72-10118. Theoretical analysis of the considered Nb/CuNi bilayer was supported by RSF Grant No. 20-69-47013. Access to scientific and technical literature and computing infrastructure was obtained by the Interdisciplinary Scientific and Educational School of Lomonosov Moscow State University “Photonic and Quantum technologies. Digital medicine”, V.S. is grateful for support for the thin films sputtering from the Ministry of Science and Higher Education of the Russian Federation (No. FSMG-2021-0005). V.S. and D.R. acknowledge the support of ANR grant CRYSTOP.

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(67) The induced coherent state in the N-layer is characterized by an energy gap \(\Delta_{\text{min}} < \Delta\), commonly referred to as the minigap.

(68) In calculations, the temperatures are conventionally expressed in units of energy \(T \rightarrow k_BT\), making straightforward their comparison with other energy scales.