Temperature dependent transport spin-polarization in the low Curie temperature complex itinerant ferromagnet EuTi$_{1-x}$Nb$_x$O$_3$

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Received 8 April 2019, revised 4 June 2019
Accepted for publication 25 June 2019
Published 15 July 2019

Abstract

The physical systems with ferromagnetism and ‘bad’ metallicity hosting unusual transport properties are playgrounds of novel quantum phenomena. Recently EuTi$_{1-x}$Nb$_x$O$_3$ emerged as a ferromagnetic system where non-trivial temperature dependent transport properties are observed due to coexistence and competition of various magnetic and non-magnetic scattering processes. In the ferromagnetic state, the resistivity shows a $T^2$ temperature dependence possibly due to electron–magnon scattering and above the Curie temperature $T_C$, the dependence changes to $T^{3/2}$ behaviour indicating a correlation between transport and magnetic properties. In this paper, we show that the transport spin-polarization ($P_t$) in EuTi$_{1-x}$Nb$_x$O$_3$, a low Curie temperature ferromagnet, is as high ($\sim$40%) as that in some of the metallic ferromagnets with high Curie temperatures. In addition, owing to the low Curie temperature of EuTi$_{1-x}$Nb$_x$O$_3$, the temperature ($T$) dependence of $P_t$ could be measured systematically up to $T_C$ which revealed a proportionate relationship with magnetization $M_s$ versus $T$. This indicates that such proportionality is far more universally valid than the ferromagnets with ideal parabolic bands. Furthermore, our band structure calculations not only helped to understand the origin of such high spin polarization in EuTi$_{1-x}$Nb$_x$O$_3$ but also provided a route to estimate the Hubbard $U$ parameter in complex metallic ferromagnets in general using experimental inputs.

Keywords: correlated electron system, complex itinerant ferromagnet, spin-polarization

(Some figures may appear in colour only in the online journal)
this context, EuTi$_{1-x}$Nb$_x$O$_3$ is found to be the ideal candidate because it is a ‘bad’ metal and at the same time, a ferromagnet with low $T_C \sim 9.5$ K for $x = 0.15$ [4].

EuTi$_{1-x}$Nb$_x$O$_3$ is an important member of the perovskite titanate family RTO$_3$ (R = rare earth ion), where Ti usually has 3$d^1$ electronic configuration. This family has attracted researchers since last two decades owing to their several fascinating properties including magnetic, dielectric and superconducting properties that have been reported for the perovskite family [5]. RTO$_3$ family also exhibits superior thermoelectric properties. Some of the most interesting properties are orbital ordering (LaTiO$_3$), orbital liquid state (YTiO$_3$) depending on the radius of R ions [5–7]. There has been a considerable amount of theoretical and experimental work done for understanding the nature of the ground state in this family [7–10]. The details of such prior work can be found in an earlier publication [4]. Among the perovskites, EuTiO$_3$ with unique divalent rare-earth ion Eu and tetravalent Ti has generated substantial interest since the discovery of magnetoelectric coupling in this compound below the antiferromagnetic (AFM) transition temperature $T_N = 5.5$ K [11–16]. EuTiO$_3$ has a positive Curie–Weiss constant and exhibits strong coupling between magnetic ordering and phonon modes. Efforts have been made to drive this system from AFM phase to other magnetic phases upon modifications due to partial substitution at the Ti site. Small amount of substitution at Ti site by Nb drives the system from AFM to ferromagnetic [16]. Substitution by Nb$^{4+}$ ion at the Ti$^{3+}$ results in the introduction of electrons in EuTiO$_3$ without disturbing the Eu$^{2+}$ moment chain. Previous studies in EuTi$_{1-x}$Nb$_x$O$_3$ revealed notable increase in electrical conductivity and large values of magnetocaloric response of about 23.8 J kg$^{-1}$ K$^{-1}$ even at low magnetic field 0–2 T [14]. However, introduction of Nb in AFM EuTiO$_3$ results in ferromagnetic behaviour in EuTi$_{1-x}$Nb$_x$O$_3$ ($x = 0.15$) with $T_C \sim 9.5$ K and saturation magnetization at 2 K is estimated to be $\sim 7 \mu_B$/Eu [14].

In this paper, we have employed spin-resolved Andreev reflection (PCAR) spectroscopy using conventional superconducting tip of Nb to measure the transport spin-polarization in EuTi$_{1-x}$Nb$_x$O$_3$ ($x = 0.15$) [17–25]. Spin polarization ($P$) in a metallic ferromagnet is generally defined as \[ P = \langle N_{\uparrow}(E_F) - N_{\downarrow}(E_F) \rangle / \langle N_{\uparrow}(E_F) + N_{\downarrow}(E_F) \rangle, \] where $N_{\uparrow}(E_F)$ and $N_{\downarrow}(E_F)$ are the density of states (DOS) of the up and down spin channels respectively at the Fermi level. However, in a transport experiment like PCAR, the relevant quantity is not the absolute spin polarization but the so called ‘transport spin polarization’ which is defined as \[ P_t = \langle (N_{\uparrow}v_{\uparrow})_{FS} - (N_{\downarrow}v_{\downarrow})_{FS} \rangle / \langle (N_{\uparrow}v_{\uparrow})_{FS} + (N_{\downarrow}v_{\downarrow})_{FS} \rangle \] in the ballistic regime, where $N_{\uparrow}$ and $N_{\downarrow}$ are the DOS of the up and down spin channels respectively at the Fermi level and $v_{\uparrow}$ and $v_{\downarrow}$ are the respective Fermi velocities [26].

PCAR spectroscopy measurements were performed on single-crystals of EuTi$_{0.85}$Nb$_{0.15}$O$_3$ using Nb tips. The polycrystalline EuTi$_{1-x}$Nb$_x$O$_3$ ($x = 0.15$) powder samples were first prepared by the conventional solid-state reaction method using high-purity Eu$_2$O$_3$, Nb$_2$O$_5$, and TiO$_2$. To remove any adsorbed CO$_2$ and H$_2$O, the rare earth oxide Eu$_2$O$_3$ was heated at 900 °C for overnight before using it. The stoichiometric mixture of the above mentioned ingredients were heated at 1000 °C–1100 °C for few days in the reduced atmosphere of 5% H$_2$ and 95% Ar, with intermediate grindings. Then, the obtained polycrystalline powder was reground and pressed into two cylindrical feed and seed rods under hydrostatic pressure. These two rods were finally sintered at 1100 °C in the same environment for 24h. The single crystal of EuTi$_{1-x}$Nb$_x$O$_3$ ($x = 0.15$) were grown under the same reduced atmosphere using a 4-mirror float zone image furnace FZ-T-10000-H-VPM (Crystal System Co.). Over the entire crystal growth, the feed and seed rods were oppositely rotated at a speed 25rpm and the typical growth rate was 5 mm h$^{-1}$.

The phase purity of EuTi$_{1-x}$Nb$_x$O$_3$ was checked by the powder XRD method with Cu$K_{\alpha}$ radiation ($\lambda = 1.5406 \AA$) in a high resolution Rigaku diffractometer (TTRAX III) at room temperature. No impurity peak has been found within the resolution of XRD which confirms the single phase nature of the compound. All the peaks in XRD were assigned to cubic structure of space group Pm3m by the Reitveld method using FULLPROF. The estimated lattice parameters $a = b = c = 3.929$ Å are very close to that reported earlier. Crystalinity was also confirmed by single crystal XRD pattern. The temperature and field dependence of the dc magnetization measurements were carried out in a SQUID-VSM [4].

The ballistic point-contacts between the sample and the tips were fabricated and controlled by moving the tip up and down by rotating a differential screw-based head assembly manually. The measurements involved obtaining the point contact spectra (i.e. differential conductance $dI/dV$ versus $V$ curves) for different contacts with different values of $Z$, the surface transparency as in the Blonder–Tinkham–Klapwijk (BTK) theory. The spectra thus obtained were analyzed using BTK theory modified to incorporate the effect of spin-polarized bands [27, 28].

In figures 1(a)–(c) we show three representative PCAR spectra (red points). The overall spectral features indicate that the point contacts belong to the ballistic or diffusive regime of transport where the two peaks symmetric about $V = 0$ appear due to Andreev reflection across a superconducting interface with finite transparency ($Z$). The black lines show the fits to the experimentally obtained spectra using spin-polarized BTK theory. The superconducting gap $\Delta$ ranges between 1.2–1.5 meV for different contacts. The extracted values of spin-polarization $P_t$ and $P$ are also shown. For different values of $Z$ between 0.265–0.388 the transport spin polarization is measured to be around 41%. The extracted values of $P_t$ is also seen to slightly depend (linearly) on $Z$ as shown in figure 1(d). The solid lines in figure 1(d) show linear extrapolation of the $Z$-dependence of $P_t$ to $Z = 0$ which gives the expected intrinsic value of the spin-polarization (for $Z = 0$).

The intrinsic spin-polarization extracted in this case is found to be approximately 45% which is comparable to elemental ferromagnetic metals like Fe ($P = 40\%$), Co ($P = 42\%$) and Nickel ($P = 39\%$). [29].

Figure 2(a) shows temperature dependence of normalized $dI/dV$ spectra for point-contacts on EuTi$_{0.85}$Nb$_{0.15}$O$_3$. The dip
at \( V = 0 \) in the spectra is maximum at the lowest observed temperature of 1.98 K. With increase in temperature, the differential conductance spectra gradually undergo thermal smearing. At temperatures greater than 8.34 K the most dominant feature of the spectra, namely, the two peaks in the conductance spectra associated with the superconducting energy gap gets flattened.

The BTK fits of the temperature dependence of normalized \( \frac{dI}{dV} \) spectra (solid line in figure 2(a)) give an estimate of temperature dependence of the measured transport spin-polarization \( P_t \) and also the broadening parameter \( \Gamma \) as shown in figure 2(b). Transport spin-polarization decreases with increase in temperature whereas the parameter \( \Gamma \) is observed to increase with temperature. \( \Gamma \) gradually increases and reaches a maximum value of 0.4 meV at 8 K close to the \( T_C \) of EuTi\(_{0.85}\)Nb\(_{0.15}\)O\(_3\). The parameter \( \Gamma \) is associated with lifetime \( (\tau) \) of superconducting quasiparticle in the way \( \Gamma = h/\tau \). The increase in \( \Gamma \) with temperature signifies a corresponding decrease in quasiparticle lifetime at the same temperature which might be due to enhanced spin fluctuations at higher temperatures. Figure 3 shows temperature dependence of transport spin-polarization and spontaneous magnetization in the same panel for a direct comparison between the two. \( P_t \) is observed to decrease with temperature following the same behaviour as \( M_s \). This is clearly seen in the inset of figure 3 where \( M_s \) and \( P_t \) are seen to linearly dependent on each other. This is remarkable because such proportional dependence of \( P_t \) and \( M_s \) with temperature is expected only for materials with strictly parabolic bands and EuTi\(_{0.85}\)Nb\(_{0.15}\)O\(_3\) is known to be a system with large correlation effects [18].

To gain insight into the experimental results, we have performed first-principles calculations within the density functional theory as implemented in the VASP [30–33]. The spin-polarized wavefunctions are described within the projector augmented wave formalism with 550 eV cutoff for the kinetic energy [34]. The exchange-correlation energy is described with the Perdew–Burke–Ernzerhof functional [35]. The strong electron correlation in Eu-4\( f \), Ti-3\( d \), and Nb-4\( d \) electrons is accounted by an on-site Hubbard-type Coulomb interaction \( U \) within the rotationally invariant Dudarev’s approach [36]. While a \( \sqrt{2} \times \sqrt{2} \times 2 \) tetragonal supercell is used to determine the correct magnetic ground state of pure EuTiO\(_3\), a \( 2\sqrt{2} \times 2 \times 2 \) orthorhombic supercell is used to determine the electronic structure and spin transport.
polarization in EuTi_{1-x}Nb_xO_3. The Brillouin zone is sampled with 4 × 8 × 6 k-point mesh according to the Monkhorst-Pack scheme [37], while the atomic positions, volume and the shape of the supercell are optimized until all the force components are less than 0.01 eV Å⁻¹. The calculated lattice parameter of 3.97 Å for EuTiO_3 compares well with the experimental value of 3.91 Å [12].

In agreement with the previous experimental and theoretical results, the present DFT + U (U_{Eu} = 3.5 and U_{Ti} = 2 eV) calculations predict an AFM insulating ground state for EuTiO_3 [38, 39]. The AFM superexchange between the half-filled 4f states of Eu^{2⁺} (S = 7/2) via the Ti-3d states wins over the ferromagnetic (FM) indirect exchange via Eu-5d states [40]. The competing FM state lies only 1.2 meV f.u.⁻¹ higher in energy. Thus, within the DFT + U approach, the tuneable Hubbard U parameter dictates the long-range magnetic ordering [41, 42]. In the absence of an on-site Coulomb interaction for the Ti-3d electrons, the U_{Eu} above 5 eV favours the competing FM state. In contrast, while U_{Ti} = 2 eV is used, a lower U_{Eu} < 4 eV describes the AFM ground state correctly. Such decrease in U_{Eu} with an onset of U for the Ti-3d electrons is suggestive, since, if the Ti electrons are assumed to be more localized then the Eu electrons need to be more delocalized in order to maintain the superexchange interaction described above. The long-range AFM order can be tuned to FM through strain, pressure, and chemical doping [16, 39]. It is known that upon doping EuTiO_3 with more than 5% Nb in place of Ti in EuTi_{1-x}Nb_xO_3, the magnetic structure changes from AFM to FM [16]. The Nb atoms in the lattice introduce one itinerant electron per Ti-atoms replaced, and as a result, EuTi_{1-x}Nb_xO_3 becomes metallic. The itinerant Nb-4d electrons mediate the Ruderman–Kittel–Kasuya–Yoshida exchange interaction between the Eu^{2⁺} ions, and the FM ground state emerges [4].

The EuTi_{1-x}Nb_xO_3 with x = 0.125 (U_{Eu} = 3.5 and U_{Ti/Nb} = 2 eV) shown in figure 4(a) becomes FM metal (figure 4(b)), and we estimate the transport spin polarization in the ballistic limit. The magnetic moment of 6.85 µB at the Eu-site is in agreement with an earlier experiment [38], which arises from the localized Eu-4f orbitals (figure 4(b)), which are around 0.5 eV below the Fermi level. A deeper investigation into the DOS indicates that the states at the Fermi level E_F is composed of Ti-3d states with small contributions from the Eu-4f and Nb-4d states (figure 4(b)). The spin-polarized DOS at the E_F is calculated to be N(u/E_F) = 0.574 states/eV/ unit-cell which is 68% higher than the N(d/E_F). The average fermi velocity is given as \langle v_F \rangle = \frac{1}{\pi} \frac{(4\pi)}{(2\pi)}. For the spin-up channel, \langle v_{F\uparrow} \rangle = 3.47 \times 10^5 m s⁻¹ which is higher than that of the spin-down channel, \langle v_{F\downarrow} \rangle = 1.99 \times 10^5 m s⁻¹. These result in a very high transport spin polarization of 49% in the ballistic regime, which is in excellent agreement with the present experimental results with x = 0.15.

It is important to discuss that the electronic structure and the concurrent P, crucially depend on the on-site Coulomb interaction U_{Eu/Ti/Nb}, which is treated as a parameter within the DFT + U formalism [43]. We find that with increasing U_{Eu}

**Figure 2.** (a) Normalized dI/dV spectra with varying temperature over a temperature range of 1.98 K to 9.33 K for point-contacts on EuTi_{0.85}Nb_{0.15}O_3 using a Nb tip. The colored lines show experimental data points and the black lines show BTK fits with spin-polarization included. (b) Temperature dependence of transport spin-polarization and the broadening parameter 1'. The solid lines are guide to the eye.

**Figure 3.** Temperature dependence of transport spin-polarization (P) and spontaneous magnetization M_s(T) normalized by that at T = 0 K in the temperature range 2–9 K. Inset shows variation of normalized magnetization with transport spin-polarization. The solid lines are guide to the eye.
(figure 4(c)) both the channels are pushed down in energy and the corresponding $P_t$ monotonically decreases to reach 25% for $U_{\text{fu}} = 5$ eV, while the $U_T$ is kept fixed at 2 eV. In contrast, with increasing $U_{\text{fu}}$ (figure 4(d)), the minority channel is pushed higher in energy and the corresponding $P_t$ increases monotonically. Ultimately a half-metallic solution emerges for $U_T = 3$ eV with 100% spin polarization. Thus, in the absence of a first-principles estimation of Hubbard $U$, one can use the experimental knowledge of transport spin polarization to better estimate the theoretical $U$ parameter in ferromagnetic metals.

In conclusion, we report point contact Andreev reflection spectroscopy on single-crystalline EuTi$_{1-x}$Nb$_x$O$_3$. EuTi$_{0.85}$Nb$_{0.15}$O$_3$ is ferromagnetic with Curie temperature $T_C = 9.5$ K. Transport spin polarization ($P_t$) estimated from differential conductance spectra is about 45% which is close to elemental ferromagnets. Temperature dependence of transport spin polarization closely follows the temperature dependence of spontaneous magnetization ($M_S$). Furthermore, temperature dependence of the broadening parameter ($\Gamma$) estimated from PCAR spectra increases with temperature. This implies, with increase in temperature, superconducting quasiparticle lifetime decreases. This decrease can be attributed to the effect of spin fluctuations close to the critical temperature of the ferromagnetic system. Thus, our study can provide an alternative way to probe spin fluctuations in ferromagnetic materials. Based on a comparative analysis between the experimental and theoretical investigations we have also discussed a possible route to directly estimate the Hubbard $U$ parameter in complex metallic ferromagnets in general.

Acknowledgments

GS acknowledges financial support from the research grants of (a) Swarnajayanti fellowship awarded by the Department of Science and Technology (DST), Govt. of India under the Grant No. DST/SJF/PSA-01/2015-16 and (b) from SERB under the Grant No. EMR/2015/001650. MK acknowledges funding from the Science and Engineering Research Board through Nano Mission project SR/NM/TP-13/2016.

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References

[1] Zutic I, Fabian J and Das Sarma S 2004 Rev. Mod. Phys. 76 323
[2] Prinz G A 1995 Phys. Today 48 58
[3] Daughton J M, Pohm A V, Fayfield R T and Smith C H 1999 J. Phys. D: Appl. Phys. 32 R169
[4] Roy S, Khan N and Mandal P 2015 Phys. Rev. B 98 134428
[5] Holdern A B and Khler J 2015 J. Phys. Chem. Solids 84 2–15
[6] Imada M, Fujimori A and Tokura Y 1998 Rev. Mod. Phys. 70 1039
[7] Ulrich C, Gssling A, Grninger M, Guennou M, Roth H, Cwik M, Lorenz T, Khaliullin G and Keimer B 2006 Phys. Rev. Lett. 97 157401
[8] Zhao Z Y, Khosravani O, Lee M, Balicas L, Sun X F, Cheng J G, Brooks J, Zhou H D and Choi E S 2015 Phys. Rev. B 91 161106
[9] Khaliullin G and Okamoto S 2002 Phys. Rev. Lett. 89 167201
[10] Hemberger J et al 2003 Phys. Rev. Lett. 91 066403
[11] Katsufuji T and Tokura Y 1999 Phys. Rev. B 60 R15021
[12] Katsufuji T and Takagi H 2001 Phys. Rev. B 64 054415
[13] Takahashi K S, Onoda M, Kawasaki M, Nagaosa N and Tokura Y 2009 Phys. Rev. Lett. 103 057204
[14] Roy S, Khan N and Mandal P 2016 APL Mater. 4 026102
[15] Li L, Morris J R, Koehler M R, Dun Z, Zhou H, Yan J, Mandrus D and Keppens V 2015 Phys. Rev. B 92 024109
[16] Li L, Zhou H, Yan J, Mandrus D and Keppens V 2014 APL Mater. 2 110701
[17] Kamboj S, Das S, Sirohi A, Chowdhury R R, Gayen S, Maurya V K, Patnaik S and Sheet G 2018 J. Phys.: Condens. Matter 30 355001
[18] Mukhopadhyay S, Raychaudhuri P, Joshi D A and Tomy C V 2007 Phys. Rev. B 75 014504
[19] Ji Y, Strijkers G J, Yang F Y, Chien C L, Byers J M, Anguelouch A, Xiao G and Gupta A 2001 Phys. Rev. Lett. 86 5585
[20] Valentine J M and Chien C L 2006 J. Appl. Phys. 99 08P902
[21] Wang L, Unemoto K, Wentzcovitch R M, Chen T Y, Chien C L, Checkelsky J G, Eckert J C, Dahlberg E D and Leighton C 2005 Phys. Rev. Lett. 94 056602
[22] Clowes S K, Miyoshi Y, Bugoslavsky Y, Branford W R, Grigorescu C, Manea S A, Monnerneau O and Cohen L F 2004 Phys. Rev. B 69 214425
[23] Panguluri R, Tsoi G, Nadgorny B, Chun S H, Samarth N and Mazin I I 2003 Phys. Rev. B 68 201307
[24] Singh S, Sheet G, Raychaudhuri P and Dhar S K 2006 Appl. Phys. Lett. 88 022506
[25] Sheet G, Rosner H, Wirth S, Leithe-Jasper A, Schnelle W, Burkhardt U, Mydosh J A, Raychaudhuri P and Grin Y 2005 Phys. Rev. B 72 180407
[26] Mazin I I 1999 Phys. Rev. Lett. 83 1427
[27] Strijkers G J, Ji Y, Yang F Y, Chien C L and Byers M 2001 J. Phys. Rev. B 63 104510
[28] Blonder G E, Tinkham M and Klapwijk T M 1982 Phys. Rev. B 25 4515
[29] Soulen R J Jr et al 1998 Science 282 85
[30] Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864
[31] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
[32] Kresse G and Hafner J 1993 Phys. Rev. B 47 558
[33] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[34] Blöchl P E 1994 Phys. Rev. B 50 17953
[35] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[36] Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Phys. Rev. B 57 1505
[37] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[38] McGuire T R, Shafer M W, Joenk R J, Alperin H A and Pickart S J 1966 J. Appl. Phys. 37 981
[39] Lee J H 2010 Nature 466 954
[40] Akamatsu H, Kumagai Y, Oba F, Fujita K, Murakami H, Tanaka K and Tanaka I 2011 Phys. Rev. B 83 214421
[41] Ranjan R, Nabi H S and Pentcheva R 2007 J. Phys.: Condens. Matter 19 406217
[42] Birol T and Fennie C J 2013 Phys. Rev. B 88 094103
[43] Anisimov V I, Zaanen J and Andersen O K 1991 Phys. Rev. B 44 943