Evidence for *s*-wave superconductivity in noncentrosymmetric Re$_{24}$Nb$_5$ from ^{93}Nb NMR measurements

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We report a ^{93}Nb nuclear magnetic resonance (NMR) study on the noncentrosymmetric superconductor Re$_{24}$Nb$_5$. Below the superconducting temperature $T_c(H)$, the spin susceptibility probed by the ^{93}Nb NMR Knight shift gradually decreases with lowering temperature, accompanied by the broadening of the resonance spectrum. Such behavior is commonly observed in the BCS-type superconductors. The ^{93}Nb NMR spin-lattice relaxation rate ($1/T_1$) shows a well-defined coherence peak just below $T_c(H)$, followed by a marked decrease with further decreasing temperature. Moreover, the $1/T_1$ data in the superconducting state were found to obey a single exponential expression, yielding a nodeless gap $\Delta/k_B = 10.3$ K. This value gives the ratio of $2\Delta/k_B T_c(H) = 3.55$, that is almost identical with the value of 3.5 predicted from BCS theory. On these bases, we conclude that the noncentrosymmetric Re$_{24}$Nb$_5$ compound can be characterized as a weakly coupled BCS-type superconductor.

I. INTRODUCTION

There is general agreement from intense experimental and theoretical research that the antisymmetric spin-orbit coupling (ASOC) will be enhanced in the superconducting (SC) materials where the atomic sites have a lack of spatial inversion symmetry.[1–4] Such enhancement would lead to the lifting of spin degeneracy and the splitting of the energy bands. Consequently, the superconducting order parameter does not have definite parity but may appear as a mixture of the spin-singlet and spin-triplet states.[1–4] Superconductors, such as CePt$_3$Si, Mg$_{12}$Ir$_{19}$B$_{15}$, Li$_2$Pt$_3$B, Re$_3$W, Mo$_3$Al$_2$C, CaIrSi$_3$, etc.,[5–13] have been reported to possess noncentrosymmetric characteristics. Among these rare-earth and transition metal based noncentrosymmetric superconductors, the *d*-electron systems are more suitable for exploring the issue of inversion symmetry breaking because the strong electron correlations in *f*-electron contained materials usually complicate the superconducting properties.

Re$_{24}$Nb$_5$, although its superconductivity was discovered four decades ago,[14,15] has been recognized as a noncentrosymmetric superconductor based on the recent study of the nearly stoichiometric compound Re$_{0.82}$Nb$_{0.18}$ (equivalent to Re$_{23.8}$Nb$_{5.2}$) by Karki and coworkers.[16] This material crystallizes in the Re$_{24}$Ti$_5$-type structure with the space group $I\bar{4}3m$ (No. 217). Within this crystal structure, there are two nonequivalent crystallographic niobium sites and two rhenium sites in Re$_{24}$Nb$_5$. Among them, only the Nb(1) site (2a in Wyckoff notation) displays an inversion center. Since the Re atom is a heavy element, the effect of ASOC is expected to be strong in Re$_{24}$Nb$_5$. This would provide an opportunity for the searching for the existence of a mixture of the spin-singlet and spin-triplet states in the SC phase of this compound.

In this Brief Report, we present the results of a ^{93}Nb nuclear magnetic resonance (NMR) study in the normal and superconducting states of Re$_{24}$Nb$_5$. The spin-lattice relaxation rate ($1/T_1$) data were found to exhibit a constant T_1T relationship in the normal state and a rapid decrease in the SC state, accompanied by the presence of a distinct coherence peak just below the SC transition temperature $T_c(H)$. These

observations are in agreement with an *s*-wave model with a single nodeless gap $\Delta/k_B \simeq 10.3$ K. This result yields $2\Delta/k_B T_c(H) = 3.55$, almost identical with the BCS value of 3.5, suggesting a weakly coupled BCS-type superconductivity for Re$_{24}$Nb$_5$.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A nominally stoichiometric Re$_{24}$Nb$_5$ sample was prepared from 99.997% Re and 99.95% Nb by mixing appropriate amounts of elemental metals. They were placed in a water-cooled copper crucible and then were melted several times in an Ar arc-melting furnace. The resulting ingot was annealed in a vacuum-sealed quartz tube at 800 °C for 5 days, followed by furnace cooling. A room-temperature x-ray diffraction taken with Cu K_α radiation on the powdered sample is shown in Fig. 1. It is seen that the diffraction spectrum in this material was identical to the expected Re$_{24}$Ti$_5$-type structure. In a more detailed analysis of the x-ray data, the $I\bar{4}3m$ phase was refined with the Rietveld method. We thus extracted the lattice constant $a = 9.6076$ Å for our Re$_{24}$Nb$_5$. This value is a bit smaller than that of Re$_{23.8}$Nb$_{5.2}$ ($a = 9.6293$ Å),[16] in agreement with the fact that Nb has a larger atomic size than Re.

DC magnetization *M* measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer measured at a field $H_o = 10$ Oe under zero-field-cooled (ZFC) and field-cooled (FC) processes. The temperature dependence of M/H_o for Re$_{24}$Nb$_5$ is illustrated in Fig. 2. The observed diamagnetic behavior below the transition temperature $T_c \simeq 8.7$ K confirms the occurrence of superconductivity in this material. Here T_c was defined as the onset of the diamagnetic response in the magnetization data, as indicated by the arrow in Fig. 2. It is worthwhile mentioning that we prepared several specimens with slight excess Nb and Re concentrations from the stoichiometry but found minor changes on the value of T_c. Such an observation is consistent with the reported result by Karki *et al.*[16]

NMR measurements were performed using a Varian 300 spectrometer with a constant field of 6.94 T. The magnitude of T_c is reduced to $T_c(H) = 5.8$ K by such of the external
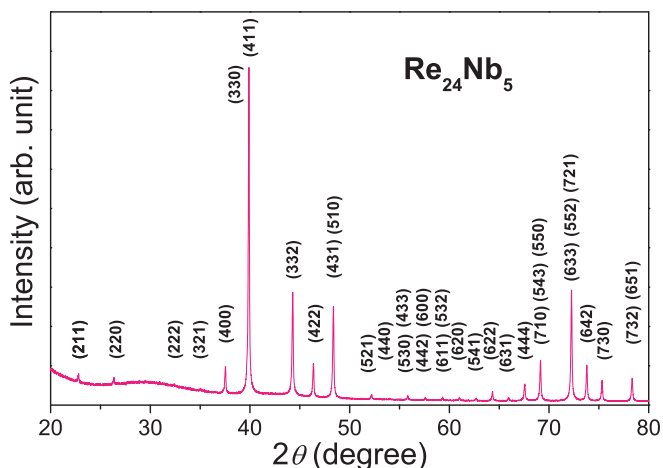
FIG. 1. (Color online) Room-temperature x-ray diffraction pattern for $Re_{24}Nb_5$. Reflections are indexed with respect to the $I\bar{4}3m$ space group.

FIG. 3. (Color online) ^{93}Nb NMR central transition line shapes of $Re_{24}Nb_5$ measured at various temperatures in a magnetic field of 6.94 T. Each spectrum is normalized to its maximum intensity for clarity.

field employed in our NMR experiment. The specimen was put in a plastic vial that showed no observable ^{93}Nb NMR signal.[17] The ^{93}Nb NMR central transition lines were obtained by the Fourier transform of a half of the spin-echo signal using a standard $\pi/2-\tau-\pi$ sequence. Within the $Re_{24}Ti_5$-type crystal structure, there are two crystallographic Nb sites, Nb(1) and Nb(2), with population ratio of 1:4. Hence, the observed ^{93}Nb NMR line shape is mainly featured by the Nb(2) site while a small hump at the higher frequency could be associated with Nb(1). Several representative spectra taken below and above 5.8 K are displayed in Fig. 3. It is apparent that the resonance line becomes broad below $T_c(H)$, typical behavior due to a spatial field modulation in the mixed state of type-II superconductors. In the inset of Fig. 4, we presented the temperature variation of the line width $\Delta \nu$, estimated from the full width at half maximum (FWHM) of the main line.

The observed temperature-dependent ^{93}Nb Knight shift (^{93}K) of $Re_{24}Nb_5$ is given in Fig. 4. Here ^{93}K was evaluated from the position of the maximum of each spectrum with respect to an aqueous $KNbCl_6$ solution reference.[18] Note
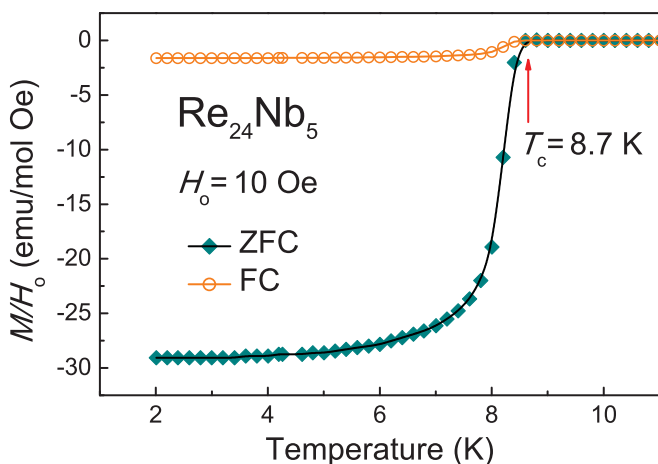
that the error bars here were taken as the accuracy for the determination of the maximum. The obtained ^{93}K is positive and shows temperature independence in a normal state, being consistent with the Pauli-type paramagnetic nature for $Re_{24}Nb_5$. The large positive ^{93}K value of about 0.41% is mainly associated with the orbital shift. Below $T_c(H)$, ^{93}K shifts to higher frequencies, indicating that the niobium d electrons play an important role for the reduction of the electronic density of states (DOS) due to the onset of superconductivity since the hyperfine field associated with the core polarization via $4d$ electrons is negative.[19–21] While associating the frequency shift with specific electronic changes is usually complicated by undistinguished s-electron, core polarization, quadrupolar, and orbital terms, the spin-lattice relaxation rate is comparatively simple due to the domination

FIG. 2. (Color online) Temperature dependence of M/H_o under zero-field-cooled and field-cooled processes for $Re_{24}Nb_5$ measured at $H_o = 10$ Oe.

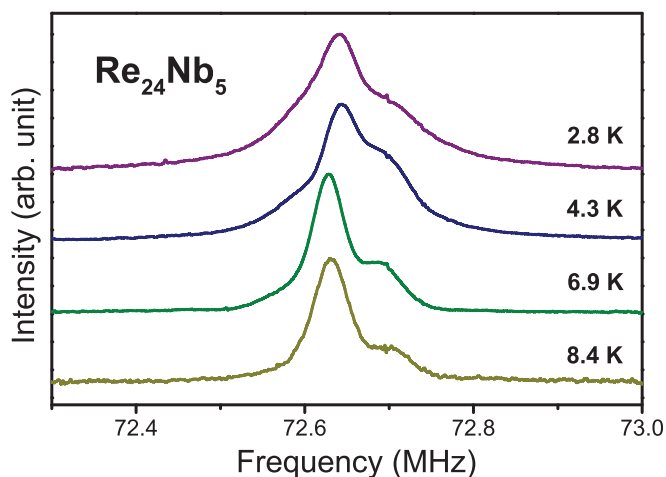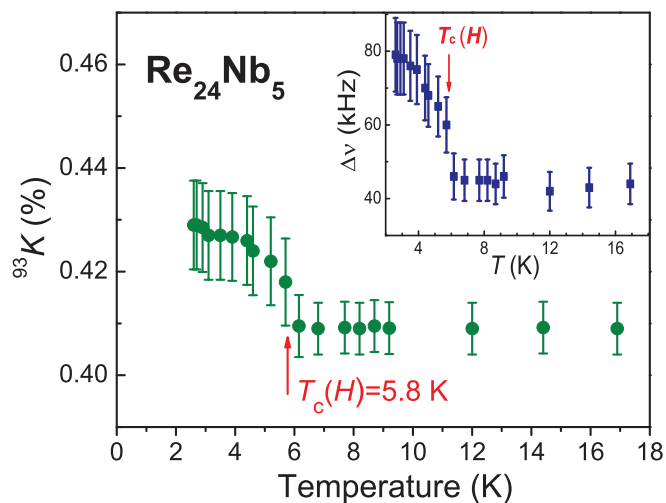FIG. 4. (Color online) Temperature dependence of the ^{93}Nb NMR Knight shift for $Re_{24}Nb_5$. Inset: the temperature variation of the line width $\Delta \nu$, estimated from the full width at half maximum of the main line.
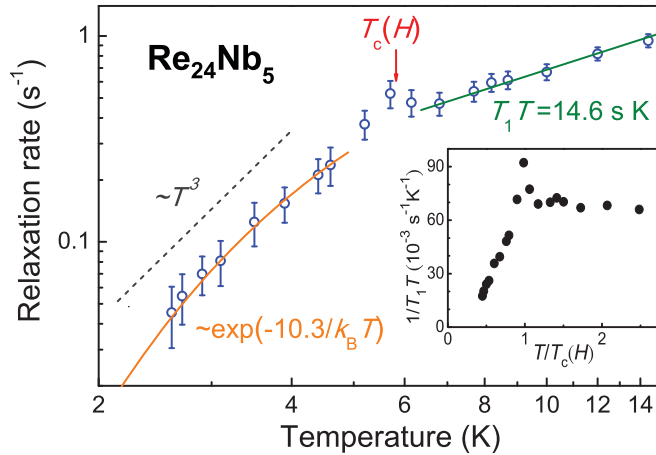
FIG. 5. (Color online) Temperature variation of the ^{93}Nb NMR spin-lattice relaxation rate for $Re_{24}Nb_5$. The solid straight line represents the Korringa behavior above $T_c(H)$. The solid curve is a fit to a single exponential expression below $T_c(H)$, yielding a gap of 10.3 K. The T^3 dependence was plotted for comparison. The inset shows the variation of $1/T_1T$ as a function of the normalized temperature $T/T_c(H)$.

by core polarization, thus providing a directly quantitative probe of electronic DOS changes.

The spin-lattice relaxation time T_1 measurement was carried out using the inversion recovery method. We recorded the signal strength by integrating the recovered spin echo signal. In these experiments, the relaxation process involves the adjacent pairs of spin levels, and the corresponding T_1 is a multiexponential expression.[22] For the central transition with $I = \frac{9}{2}$, the recovery of the nuclear magnetization m follows

$$\frac{m(t) - m(\infty)}{m(\infty)} = -2\alpha\left(0.152e^{-\frac{t}{T_1}} + 0.14e^{-\frac{6t}{T_1}} + 0.153e^{-\frac{15t}{T_1}}\right.$$
$$\left. + 0.192e^{-\frac{28t}{T_1}} + 0.363e^{-\frac{45t}{T_1}}\right). \quad (1)$$

Here $m(t)$ is the magnetization at the recovery time t, and $m(\infty)$ is the magnetization after a long time recovery. The parameter α is a fractional value derived from the initial conditions used in our experiments. Each T_1 value was thus obtained by fitting to this multiexponential recovery curve. The observed temperature dependence of $1/T_1$ for $Re_{24}Nb_5$ is depicted in Fig. 5.

Above 5.8 K, $1/T_1$ obeys the Korringa relation with a constant $T_1T = 14.6$ s K. A well-defined coherence peak (Hebel-Slichter peak)[23] appears just below $T_c(H)$, followed by a marked decrease down to 2.6 K. These characteristics are commonly observed within the BCS-type superconductors. In the inset of Fig. 5, we plotted $1/T_1T$ as a function of the normalized temperature $T/T_c(H)$, showing a more pronounced

peak feature around $T_c(H)$. It is known that the temperature variation of $1/T_1$ in the SC state is related to the SC gap structure. Evidently, the $1/T_1$ data can be fitted well to a single exponential expression from $0.82T_c(H)$ to $0.45T_c(H)$, yielding the magnitude of the SC gap $\Delta/k_B = 10.3$ K. This value gives the ratio of $2\Delta/k_BT_c(H) = 3.55$ which is similar to the value of 3.67 obtained from the analysis of the electronic heat capacity in $Re_{0.82}Nb_{0.18}$.[16] In addition, this result is also comparable to those in other fully gapped noncentrosymmetric superconductors such as 3.52 for Re_3W and 3.59 for $Mg_{10}Ir_{19}B_{16}$.[10,24]

As the SC gap possesses line nodes, the T-dependent $1/T_1$ is expected to obey T^3 behavior below $T_c(H)$ and exhibits no Hebel-Slichter peak at around $T_c(H)$. However, our $1/T_1$ reveals a distinct coherence peak near $T_c(H)$ followed by an exponential decay in $Re_{24}Nb_5$. Moreover, the revealed $2\Delta/k_BT_c(H) = 3.55$ is almost identical with the BCS value of 3.5, suggesting that $Re_{24}Nb_5$ is a weakly coupled s-wave superconductor. Hence, the NMR observation tends to indicate that the effect of the ASOC is quite weak in the current case of $Re_{24}Nb_5$. This result is very likely due to a small band splitting lifted by ASOC as compared to the relatively high transition temperature $T_c \simeq 8.7$ K for $Re_{24}Nb_5$. On the other hand, Mineev and Samokhin have argued that the effects of nonmagnetic impurities on noncentrosymmetric superconductors may lead to an inevitable consequence of the band splitting even though the intrinsic ASOC is stronger than SC energy scales.[25] If such an extrinsic effect appears in our sample, it might mask the underlying SC gap anisotropy in the present $Re_{24}Nb_5$. In this respect, a further investigation of a single crystal $Re_{24}Nb_5$ is highly desirable for solving this puzzle.

III. CONCLUSIONS

The SC characteristics of the noncentrosymmetric superconductor $Re_{24}Nb_5$ have been investigated through ^{93}Nb NMR measurements. The important findings are that the spin-lattice relaxation rate of $Re_{24}Nb_5$ exhibits a coherence peak just below $T_c(H)$ and its temperature dependence can be described by means of the s-wave BCS model. We also commented that the invisible mixture of the spin-singlet and spin-triplet states in the SC phase of this compound could be attributed to its relatively high transition temperature. However, the possible suppression of the ASOC by impurities and/or disorder should not be ruled out as using a polycrystalline $Re_{24}Nb_5$.

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