Electrical resistivity and Andreev reflection spectroscopy of the superconducting oxide spinel $LiTi_2O_4$

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We measured resistivity and Andreev reflection spectroscopy on $LiTi_2O_4$ polycrystalline samples ($T_c \approx 12.3$ K) synthesized by a new method. Resistivity shows the metallic temperature dependence and is well fitted by the Bloch-Grüneisen theory above 90 K. This is consistent with the picture of electron-phonon scattering. Below 90 K and above T_c it shows T^2 temperature dependence suggesting Fermi liquid behavior above T_c. From the $H_{c2}-T$ phase diagram the upper critical field $H_{c2}(0)$ is estimated to be about 11.6 T based on the Ginzburg-Landau theory. Point-contact Andreev reflection spectroscopy gives $2\Delta_0/k_BT_C \approx 4$ and reveals that $LiTi_2O_4$ is a typical intermediate-coupling *s*-wave BCS superconductor. We also observed the resistive hump in a normal state and the field-induced upturn near the transition region of the $\rho(T)$ curve on the aged samples. In comparison with the fresh one, it suggests that the above exotic $\rho(T)$ behavior is not an intrinsic character of the pure stoichiometric $LiTi_2O_4$ compound.

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$LiTi_2O_4$ is a spinel oxide superconductor with a transition temperature $T_c \approx 12$ K. The band structure calculation[1] indicates that the conduction band states are mainly coming from Ti 3*d* bands which lie about 2–3 eV above the O 2*p* bands, that is different from other transition-metal spinels in which *d* and *p* orbitals hybridize with each other and go across the E_f energy. Thus $LiTi_2O_4$ is a *d*-electron superconductor due to the large separation between *d* and *p* orbitals. Initially the superconductivity of $LiTi_2O_4$ is considered as due to electron-phonon coupling.[2] Some tunneling spectra experiments[3,4] revealed that $2\Delta_0/k_BT_C \approx 3.5-3.7$ or 4.00 ± 0.06, which are in good agreement with the BCS theory. Alternatively, it was suggested that the superconductivity in $LiTi_2O_4$ is possibly induced by resonating-valence-bond mechanism.[1] However, the recent specific heat experiments revealed that $LiTi_2O_4$ is a typical type-II, BCS-like, moderate coupling *s*-wave superconductor.[5]

The occurrence of a composition-induced metal-semiconductor transition in $Li_{1+x}Ti_{2-x}O_4$ was observed both in experiments[6–8] and theoretical calculations.[9] The stoichiometric $LiTi_2O_4$ ($x=0$) is a metal with a superconducting transition at 12 K and $Li_{4/3}Ti_{5/3}O_4$ ($x=1/3$) is a semiconductor. It was reported that $LiTi_2O_4$ is not stable in air and moisture, and a metal-semiconductor transition was observed in an aged sample (exposed in air for 5 days) at temperatures close to the superconducting transition region in a fresh sample.[10] Under a magnetic field the resistivity of off-stoichiometric $LiTi_2O_4$ shows an abnormal upturn near the transition region.[11,12] Surprisingly, it was observed that the $\rho(T)$ curve of the stoichiometric $LiTi_2O_4$ sample shows a strange hump in normal state as well as the off-stoichiometric compound.[8,12] Due to the volatility of Li_2O, conventional preparation of $LiTi_2O_4$ is difficult to obtain an exact composition of Li, therefore the above result needs to be confirmed.[10] In this paper, we report the result from the study on $LiTi_2O_4$ polycrystalline samples which were synthesized by a new method[13] by avoiding inexact Li content. This sample provides a way to a better understanding on the physical properties of the stoichiometric $LiTi_2O_4$.

Our high quality polycrystalline $LiTi_2O_4$ was synthesized by solid state reaction from the $Li_2Ti_3O_7$ single crystal. In contrast to the conventional method,[13] this is a new method based on the chemical reaction: $2Li_2Ti_3O_7 + 2TiO = 4LiTi_2O_4$. The starting materials are chemical reagent TiO and $Li_2Ti_3O_7$ monocrystal powders with the purities better than 99.99%. The stoichiometric powders were mixed, ground, pelletized, and calcined in an evacuated quartz tube at 805 °C for 50 h, then cooled slowly to room temperature. The lattice constants of freshly prepared samples is 8.400 ± 0.002 Å from the x-ray diffraction data.[13] The obtained fresh sample will become the aged one after being exposed to air for several days.

We measured the resistivity and Andreev reflection spectroscopy by using the Oxford multiparameter measurement system (MagLab-Exa12). The temperature dependent resistance was measured using the four-terminal technique. The point contact Andreev reflection measurements were carried out by pointing a Pt/Ir alloy tip towards the $LiTi_2O_4$ sample. Typical four-terminal and lock-in techniques were used to measure the $I-V$ curves and the differential resistance dV/dI vs V of the point contacts. Then the dynamical conductance $dI/dV \sim V$ (or $\sigma \sim V$) was obtained both by converting the $dV/dI \sim V$ curves and by calculating the derivative of $I-V$ relations in order to ensure the reliability of the results.

The temperature dependent resistivity of the fresh sample in zero field is shown in Fig. 1(a). The resistive superconducting transition is very sharp. The midpoint of the resistive transition is 12.3 K, and the resistive onset temperature is 12.5 K. The width of the superconducting transition defined as 90%–10% of the resistive transition, is less than 0.3 K. In a normal state, we observed that the slope $d\rho(T)/dT$ increases at low temperature and decreases at higher temperature but keeps positive in the whole temperature range studied here ($T < 280$K), which looks similar to that of the

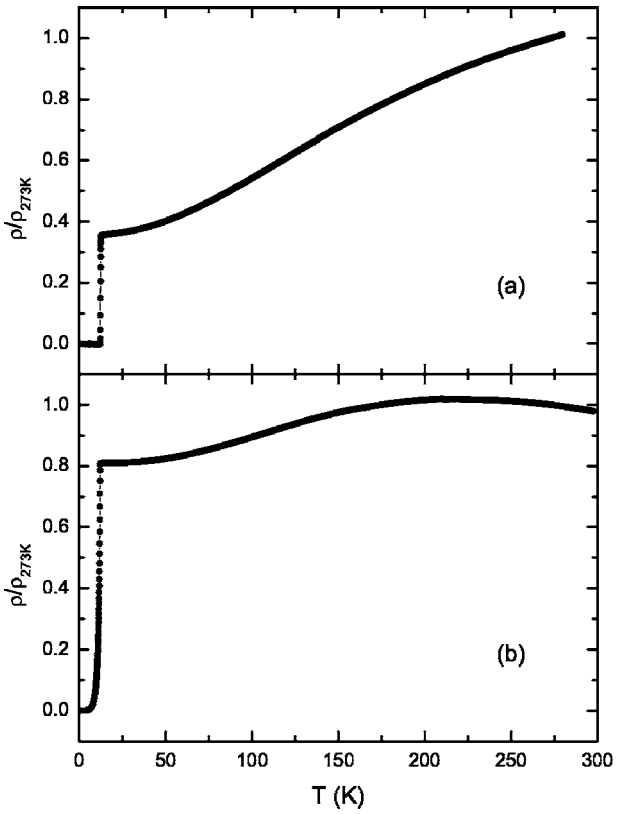

FIG. 1. Temperature dependence of resistivity (normalized by the value at 273 K) measured on $LiTi_2O_4$. (a) Fresh sample (T_c=12.3 K). We have not observed an anomalous resistivity maximum and the ρ vs T curve looks similar to that of the conventional metals dominated by electron-phonon scattering mechanism. (b) Aged sample (T_c^{on}=12.1 K). It shows a peculiar hump in a normal state due to the existence of multicomponents (see text).

conventional metals predominated by the electron-phonon scattering mechanism and is different from the linear-T dependence of the resistivity observed in high-T_c cuprate superconductors.

On this fresh stoichiometric $LiTi_2O_4$ sample, we have not found an anomalous resistivity maximum as previously reported in the works of Liao[11,12] and Heintz.[8] But for the aged sample, Fig. 1(b) shows a particular hump of the ρ vs T curve in the normal state and the onset transition temperature is 12.1 K. The aged sample has no zero resistivity down to 1.8 K and the width of the transition (defined as 10%–90% ρ_n) is 2.4 K. This result suggests that the aged sample may have more than one phase, the semiconductor $Li_{4/3}Ti_{5/3}O_4$ or the other unknown semiconductor phases may coexist with the superconducting one. On this curve, the temperature of the maximal resistivity is around 200 K that is consistent with the value observed by Heintz.[8] Moreover, for our aged sample, $\rho(300\ \mathrm{K})/\rho(T_c^{on})=1.21$ is close to the stoichiometric $LiTi_2O_4$ $[\rho(300\ \mathrm{K})/\rho(T_c^{on})=1.28]$ as reported in Ref. 6.

Since the $LiTi_2O_4$ sample is polycrystalline and very loose, air or moisture are easy to react with the interior grains leading to inhomogeneous Li content in aged samples. For the off-stoichiometric superconductor $Li_{1+x}Ti_{2-x}O_4$ $(0.04 \leqslant x \leqslant 0.12)$ the resistivity of the normal state increases

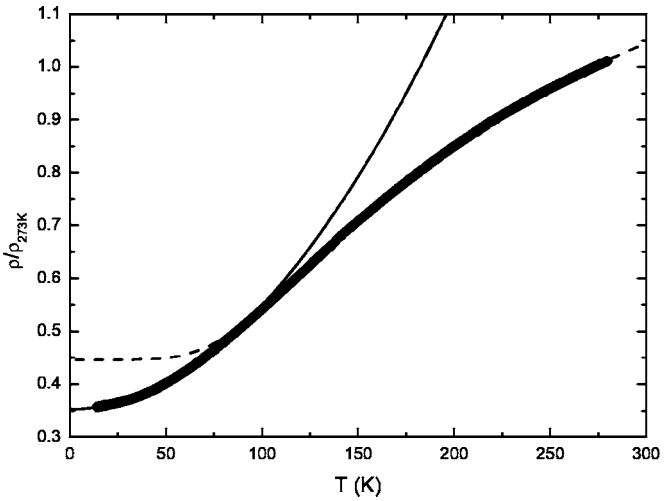

FIG. 2. Temperature dependent resistivity (normalized by the value at 273 K) of the fresh $LiTi_2O_4$ sample in normal state. The solid line is the best fitting result of $\rho(T)$ with a power law below 90 K with $\rho=\rho_0+aT^{1.986}$ supporting the Fermi liquid picture above T_c. The dashed line is the theoretical curve calculated according to the Bloch-Grüneisen expression indicating that the conventional electron-phonon mechanism is dominant above 90 K.

with decreasing temperature.[8] Therefore, the contributions from the multiphases result in a hump in the temperature dependent resistivity of the aged sample. Similarly, owing to the volatility of Li_2O, conventional preparation of $LiTi_2O_4$ may lead to inhomogeneous Li content of the samples and hence result in a resistive hump. Considering the fact that both stoichiometric and off-stoichiometric samples have almost the same superconducting transition temperature,[8] it is tempting to suggest that the resistive hump in normal state is due to the existence of multicomponents and is not an intrinsic phenomenon of the pure stoichiometric $LiTi_2O_4$ phase as presented in Fig. 1.

Because the normal-state $\rho(T)$ of this fresh sample shown in Fig. 1(a) is similar to that observed in the conventional metals, we tried to fit the $\rho(T)$ curve with the Bloch-Grüneisen expression, which is a good approximation for electron-phonon scattering in conventional metals. We use the explicit form of the Bloch-Grüneisen expression, which assumes the Einstein phonon distribution $\epsilon=k_B\Theta_E$. Subsequently, the exact result for resistivity is[14]

$$\rho^{-1} = \rho_p^{-1} + (\rho_0 + \rho_{ph})^{-1}, \tag{1}$$

$$\rho_{ph} = \rho_l \coth(\Theta_E/2T)[1 + (2/3)\sinh^2(\Theta_E/2T)]^{-1}, \tag{2}$$

where ρ_0 is a residual resistivity that is in series with ρ_{ph} and ρ_l is a constant. ρ_p is the parallel part of the impurity resistivity which is parallel with ρ_{ph} for better fitting.[15] It is found that the Bloch-Grüneisen expression can well fit the resistivity from 90 to 300 K (the fitting result is denoted by the dashed line in Fig. 2.) which is similar to the case of $MgCNi_3$ (Ref. 15) and the best fitting gives $\rho_0/\rho_{273\ \mathrm{K}}=0.578$, $\rho_p/\rho_{273\ \mathrm{K}}=1.961$, and $\Theta_E=367$ K which is reasonable compared with the Debye temperatures of 657 K derived from the specific heat measurements.[5] Hence the phonon density

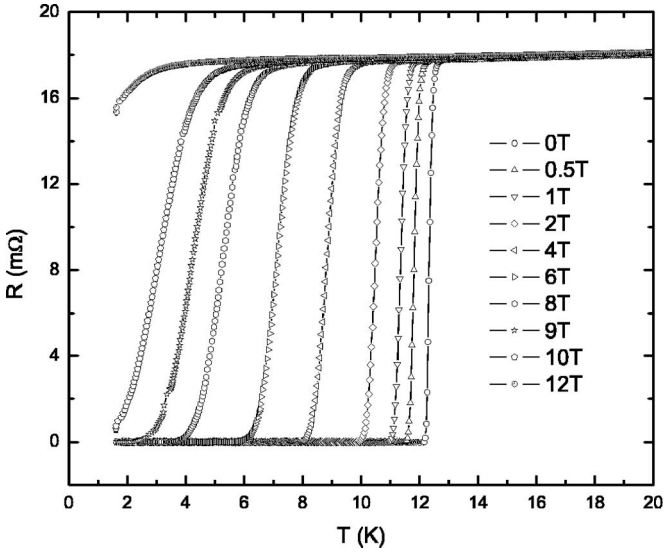

FIG. 3. The superconducting transition of the fresh $LiTi_2O_4$ sample measured at different magnetic fields. The transition curve shifts parallel down to a lower temperature with increasing field, which is similar to the conventional electron-phonon coupling superconductors.

of states should have a peak at about 32 meV considering the Einstein phonon distribution, which is consistent with the inelastic neutron scattering experimental results.[16] Below 90 K, we fitted the data to the simple power law $\rho=\rho_0+aT^n$ as indicated by the solid line in Fig. 2, yielding $n=1.986$ and $\rho_0/\rho_{273\ \mathrm{K}}=0.352$. This is in good agreement with the Fermi liquid picture above T_c. The power law is not good above 125 K because in this region the electron-phonon scattering is dominant.

In Fig. 3 we present the temperature dependent resistivity of the fresh sample under various magnetic fields up to 12 T. It was noted that by increasing the magnetic field the resistive superconducting transition shifts parallel down to lower

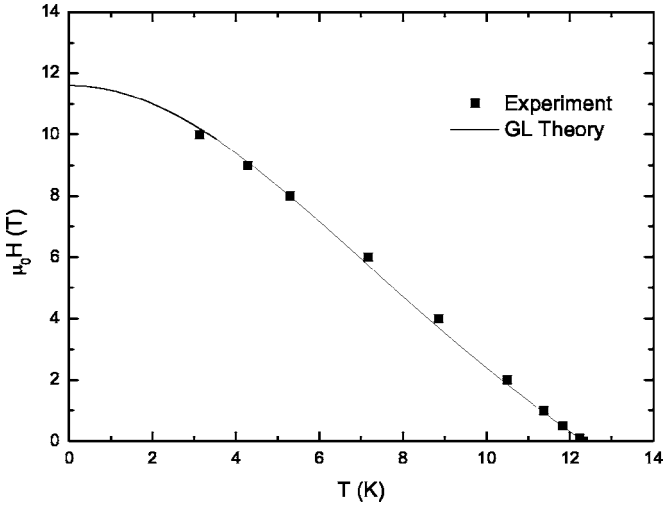

FIG. 4. The upper critical field determined from the midpoint of the superconducting transition for the fresh $LiTi_2O_4$ sample. The solid line represents the best fitting curve of the Ginzburg-Landau theory yielding $H_{c2}(0)=11.6$ T.

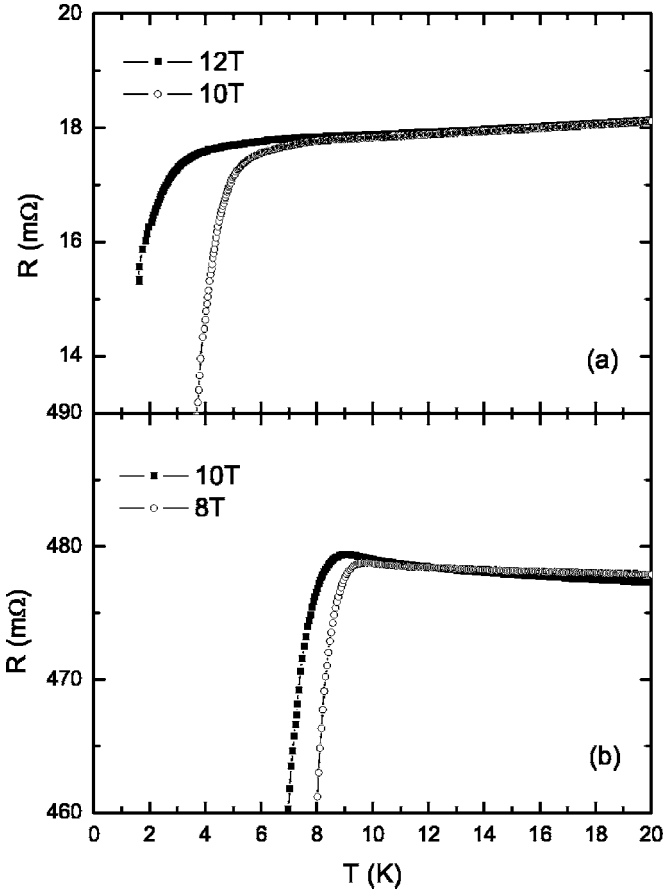

FIG. 5. Temperature dependence of resistance near the transition region under high magnetic fields. (a) Fresh sample. No resistivity minimum has been observed near the superconducting transition. (b) Aged sample. It shows an abnormal resistive upturn near the superconducting transition.

temperatures. This result is unlike the high-T_c cuprate superconductors and is similar to the conventional electron-phonon coupling superconductors such as Nb_3Sn. Figure 4 shows the $H_{c2}-T$ phase diagram obtained from the ρ vs T curves at different fields. In this figure, T_c is defined as the midpoint of the transition curves and we use the equation derived from Ginzburg-Landau theory to fit the H_{c2} data. In the Ginzburg-Landau theory, it is known that $H_{c2}=\Phi_0/2\pi\xi^2$ and $\xi\sqrt{(1+t^2)/(1-t^2)}$, where Φ_0 is the flux quanta, ξ is the coherence length, $t=T/T_c$ is the reduced temperature, and thus the upper critical field is

$$H_{c2}(T)=H_{c2}(0)\frac{1-t^2}{1+t^2}. \tag{3}$$

It was found that $H_{c2}(T)$ can be well fitted by the above expression yielding $H_{c2}(0)=11.6$ T. Further more the temperature dependence of the H_{c2} data from resistivity is consistent with that from the specific heat.[5] This analysis indicates that $LiTi_2O_4$ is a typical type-II BCS superconductor.

Figure 5 shows the temperature dependence of resistance near the transition region under a high magnetic field. For the fresh sample as shown in Fig. 3, we have not observed a

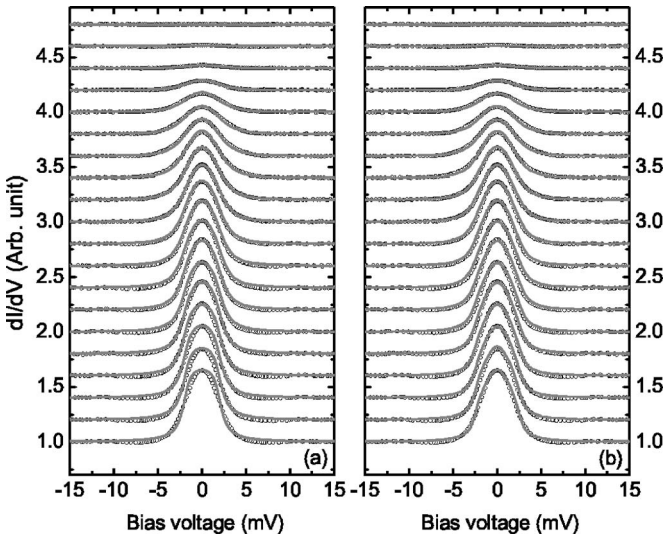

FIG. 6. The temperature dependent Andreev reflection spectra measured on the PtIr/$LiTi_2O_4$ point contact, which have been normalized by the high-bias conductance. The curves have been shifted for clarity. The corresponding temperature from the bottom up increases from 2 to 12 K with a step of 0.5 K. The solid lines denote the *s*-wave BTK simulations and the open circles are the measured Andreev reflection spectra. (a) Fitting to the isotropic *s*-wave BTK model. (b) Fitting to the anisotropic *s*-wave BTK model.

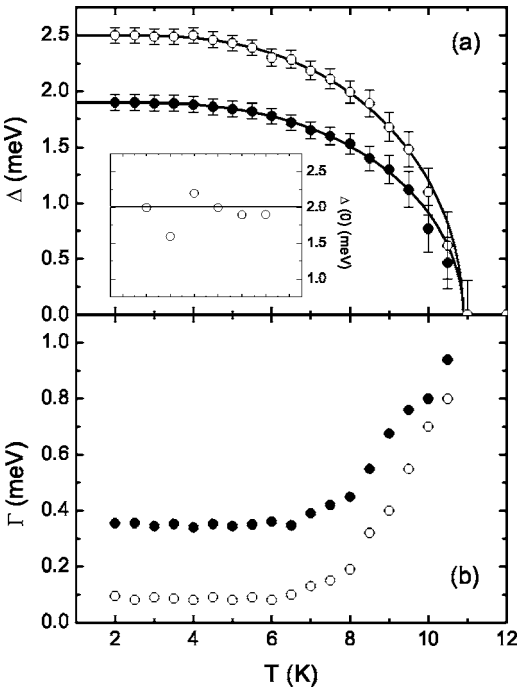

FIG. 7. (a) The temperature dependence of the superconducting gap. The solid line represents the gap predicted by the BCS theory and the solid and open circles are obtained by a fitting to the isotropic and anisotropic *s*-wave BTK theory, respectively. The inset shows the statistics of $\Delta(0)$ for different positions on the sample surface. (b) The temperature dependence of the fitting parameter Γ. The solid and open circles are determined by a fitting to the isotropic and anisotropic *s*-wave model, respectively.

broad minimum in a resistance curve near the superconducting transition under different magnetic fields, which is very different from the results of Refs. 9 and 10. While for the aged sample, an obvious abnormal upturn was observed on the $R(T)$ curve measured in a higher field, which is similar to the previous reports.[11,12] Considering that the aged sample may have some off-stoichiometric phases, we can conclude that the abnormal resistive upturn near the transition region is also not an intrinsic character of pure stoichiometric $LiTi_2O_4$.

Figure 6 shows the normalized spectra of PtIr/$LiTi_2O_4$ point contact (denoted by open circles) with a clear Andreev reflection peak at zero bias. It is noted that the characteristics of superconductivity disappear completely at about 12 K, so the backgrounds of all measured spectra are constructed from the high-bias part according to the functional form of the spectra at 12 K. Divided by such background, the measured spectrum is converted to the normalized one, which can be readily compared with the BTK theory. Meanwhile, the zero bias value on the normalized spectrum is approximately equal to the zero bias conductance relative to the high-bias one.

In the generalized BTK model,[17] two parameters are introduced to describe the necessary physical quantities, i.e., the effective potential barrier (Z) and the superconducting energy gap (Δ). As an extension, the quasiparticle energy E is replaced by $E+i\Gamma$, where Γ is the broadening parameter characterizing the finite lifetime of the quasiparticles due to inelastic scattering near the N/S microconstriction.[18,19] Because the junction resistance derived from the high-bias resistive values is approximately constant from 2 to 12 K, the barrier height Z is assumed to be constant and independent of temperature in the fitting procedure. Hence one can obtain $Z=0.12\pm0.02$ by fitting the spectrum of 2 K and applying it in the fitting for all temperatures. The fitting parameters Γ are presented in Fig. 7(b). The parameter of Γ is nearly constant below 7 K indicating the stability of the point-contact measurements. Above 7 K, the Γ value increases with increasing temperature; this may be related to the enhancement of the quasiparticle scattering by fluctuations near the critical temperature.

The ballistic formulas used here can be explained in the following discussion. From the raw data of the directional spectral measurements, the differential conductance in high bias is linear with the bias. It indicated that there is no thermal effect in our measurement, because the thermal effect would lead to a decline of the conductance at high bias. The size of the point contacts is estimated using the formulas of $R=R_0(1+Z^2)$ and $R_0=\rho l/4a^2$. Here l is the mean free path of the electron which is about 32 Å,[5] Z (≈0.1) is the barrier height, and R is the junction resistance. In this work R is between 60 and 150 Ω, so $R=100$ Ω was taken in this estimation. ρ is the resistivity of $LiTi_2O_4$ which has a value of about 1 mΩ/cm. It gives the contact diameter $a\approx90$ Å which is close to $l=32$ Å, indicating that our point-contact junctions are between the diffusive limit and the ballistic limit. Although the diffusive limit and ballistic limit have different formulas to fit the experimental data, the difference between the superconducting energy gap values derived from

TABLE I. The result of present work in comparison with the earlier reports.

Parameters	Ref. 3	Ref. 4	Ref. 5	Present work
Δ_0 (meV)	1.75–1.85	1.95±0.03	1.97	1.9
$2\Delta_0/k_BT_C$	3.5–3.7	4.00±0.06	4.0	4

the two limits is very little. The major difference is between the Z values given by these two limits.[20] Since we focused our attention on the behavior of the superconducting energy gap here, it should be reasonable to use the formula of the ballistic limit in this paper.

The solid lines in Fig. 6(a) represent the fitting results by the isotropic s-wave BTK model. As denoted by the solid circles in Fig. 7(a), the temperature dependence of the superconducting gap determinded by the fitting to s-wave isotropic BTK model is consistent with the prediction of the BCS theory. We have measured the spectra at 20 different positions on the sample surface. There are six similar curves with clear Andreev reflection peaks, which give $\Delta(0)$ varying within a small extent shown in the inset of Fig. 7(a). The other unrepeated curves, which have complex structure, are owing to the intergrain Josephson effect[21] or the aging effect at surface.

Because $LiTi_2O_4$ is unstable to the exposure in air and humidity, and the polycrystalline sample is loose, zero resistivity often cannot be achieved after being exposed to air for some time. Considering the aging effect, the superconducting property on the sample surface is usually weaker than the bulk. Hence selecting the definite T_C value ($\sim$11 K) derived from Fig. 7(a) and the $\Delta_0=1.9$ meV by fitting to the s-wave isotropic BTK model, we obtained the gap ratio of $2\Delta_0/k_BT_C\approx4$, which is close to the result from the specific heat data ($\sim$4),[5] indicating an intermediate coupling in $LiTi_2O_4$. The obtained value of the gap ratio is also close to that derived from the more detailed theoretical calculation ($\sim$3.84).[22] The calculation gives the electron-phonon coupling constant of $\lambda=0.657$ implying an intermediate coupling. For clarity, we presented in Table I the present result in comparison with the previously reported ones. All these experiments suggest that the superconductivity of $LiTi_2O_4$ can be well understood within the usual intermediate-coupling s-wave BCS-type mechanism.

We have also tried to fit the spectra using the anisotropic s-wave model with the gap function of $\Delta(\theta)=\Delta_0|\cos(2\theta)|$. The solid lines in Fig. 6(b) represent the calculated curves and the open circles in Fig. 7(a) are the determined $\Delta(T)$ relation. By comparing the magnitudes of the sum of the squared deviations between the fitted data and the trial functions (i.e., the isotropic and anisotropic ones), we found that the fitting is a little better for the anisotropic s-wave model than that of the isotropic one while the obtained $\Delta(T)$ relations from two models are similar to each other. Δ_0 ($\approx$2.5 meV) derived from a fitting to the anisotropic s-wave model is greater than the case of the isotropic one. The reason is that the isotropic gap is approximately equal to the average of the anisotropic gap in the integrating region of $\theta=[-\pi/2,\pi/2]$. Although according to the above discussions the gap anisotropy cannot be confirmed in our experiment, the $\Delta(T)$ relations derived from both the isotropic and the anisotropic model are all satisfied with the BCS theory.

In summary, we have measured the resistivity and Andreev reflection spectra of the polycrystalline $LiTi_2O_4$ samples. The temperature dependence of resistivity follows Bloch-Grüneisen theory above 90 K being consistent with the electron-phonon scattering mechanism. Meanwhile, the T^2 law is satisfied for the resistivity below 90 K suggesting the validity of the Fermi liquid picture above T_c. The upper critical field has also been determined by fitting the experimental data to the Ginzburg-Landau theory. The Andreev reflection spectrum gives $\Delta_0=1.9$ meV and $2\Delta_0/k_BT_C\approx4$. All these results support the conclusion that $LiTi_2O_4$ is a type-II intermediate-coupling s-wave BCS superconductor and a conventional metal in a normal state. In comparison with the fresh sample, we observed a resistive hump in a normal state and an abnormal upturn of $\rho(T)$ near the superconducting region under magnetic field for an aged $LiTi_2O_4$ sample. It is concluded that all these exotic $\rho(T)$ behaviors are not intrinsic characters of the pure stoichiometric $LiTi_2O_4$ but due to the inhomogeneous distribution of Li by the aged effect.

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