Evidence of *s*-wave pairing symmetry in the layered superconductor $Li_{0.68}NbO_2$ from specific heat measurements

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A high quality superconducting $Li_{0.68}NbO_2$ polycrystalline sample was prepared by deintercalation of Li ions from $Li_{0.93}NbO_2$. The field-dependent resistivity and specific heat were measured down to 0.5 K. The temperature dependence of the upper critical field is determined. A notable specific-heat jump is observed at the superconducting transition temperature $T_c \sim 5.0$ K at zero field. Below T_c, the electronic specific heat shows a thermal activated behavior and agrees well with the theoretical result for the BCS *s*-wave superconductor. It indicates that the superconducting pairing in $Li_{0.68}NbO_2$ has *s*-wave symmetry.

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The recent discovery of superconductivity in $Na_{0.3}CoO_2 \cdot 1.3H_2O$ (Ref. 1) has stimulated great interest in the investigation of physical properties of quasi-two-dimensional materials with frustrations. Among them, the layered superconductor lithium niobium oxide Li_xNbO_2 has attracted our attention.[2,3] In Li_xNbO_2, Nb atoms form a triangular lattice, similar to Co atoms in Na_xCoO_2. The superconducting transition temperature of Li_xNbO_2 is ~5.5 K, close to that of $Na_xCoO_2 \cdot H_2O$ (~4.8 K). This compound is of certain characteristics of high-T_c cuprates. There exists a strong hybridization of Nb 4*d* states with O 2*p* states, and an elevated density of oxygen states at the Fermi level.[4,5] Since many layered oxides, including high-T_c cuprates Sr_2RuO_4 and $Na_{0.3}CoO_2 \cdot 1.3H_2O$, have shown unconventional superconductivity, it is of fundamental interest to know whether the superconducting pairing of this material is conventional or unconventional.

In this paper, we report the experimental data of the field-dependent resistivity and specific-heat measurements of a high quality $Li_{0.68}NbO_2$ sample. From the data, we obtain the temperature dependence of the upper critical field and the electronic specific heat by subtracting the phonon contribution from the total specific heat. By comparison with the theoretical curves for the BCS *s*- and *d*-wave superconductors, we find that the electronic specific heat agrees very well with the *s*-wave curve. The low-temperature electronic specific heat shows a thermally activated behavior. It decays exponentially with decreasing temperature. Our results indicate that $Li_{0.68}NbO_2$ is a weak-coupling BCS *s*-wave superconductor.

As shown in Fig. 1, Li_xNbO_2 $(0 < x \leq 1)$ has a layered structure analogous to MoS_2. Along the *c* axis, the lithium planes and NbO_6 trigonal-prismatic layers are stacked alternatively.[6] In each Nb-O layer, Nb atoms form a triangular lattice, similar to that of Co atoms in Na_xCoO_2. The lithium ions occupy octahedral holes between trigonal-prismatic Nb-O layers. Under the influence of the trigonal crystal field, the Nb 4*d* energy levels split into a pattern with $d_{z^2} < d_{x^2-y^2}, d_{xy} < d_{xz}, d_{yz}$.[7] In the stoichiometric compound $LiNbO_2$, the d_{z^2} band is completely occupied, the unoccupied part of conducting band is well separated from the lower one by 1.5 eV.[7–10] So it exhibits semiconducting behavior at low temperatures. However, in Li_xNbO_2 with partial removal of lithium, the conduction band that contain holes is formed.[8] The metallic behavior is observed and superconductivity occurs with T_c of ~5 K.

The burgundy-red polycrystalline $LiNbO_2$ was synthesized by heating Li_3NbO_4 and NbO in a molar ratio of 1:2 in an evacuated fused-silica tube at 1050 °C for 60 h. Pressed pellets of the reaction mixture were wrapped in a niobium sheet to avoid reacting with the quartz. Li_3NbO_4 was obtained by heating a mixture of Li_2CO_3 and Nb_2O_5 in a molar ratio of 3:1 at 900 °C in air for 48 h, and NbO was prepared

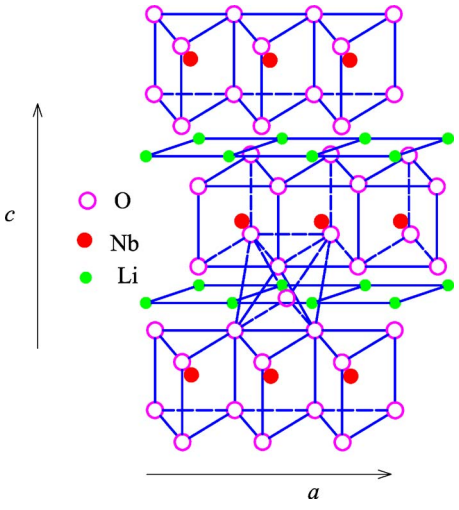

FIG. 1. (Color online) Schematic crystal structure of $LiNbO_2$ (from Ref. 2). The lithium ions (small open circles) occupy the octahedral holes between trigonal-prismatic Nb-O layers. The niobium (solid circles) and oxygen ions (large open circles) form NbO_6 trigonal prisms.

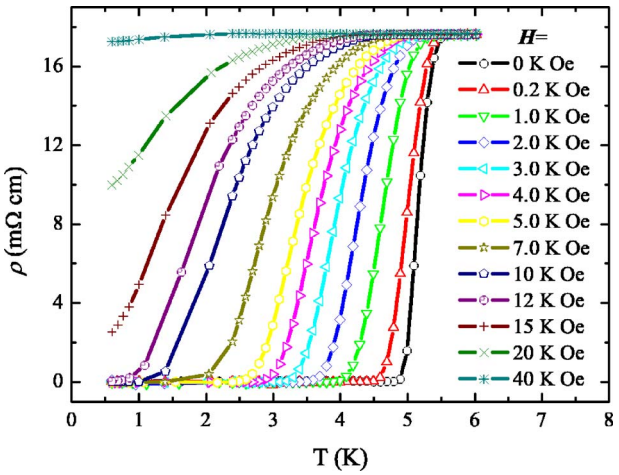

FIG. 2. (Color online) Temperature dependence of the resistivity $\rho(T)$ for $Li_{0.68}NbO_2$ at different magnetic fields.

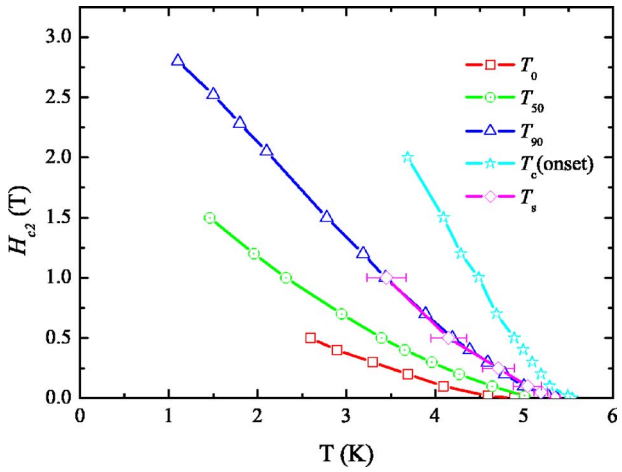

FIG. 3. (Color online) Temperature dependence of upper critical fields determined from the resistivity [denoted by T_0, T_{50}, T_{90}, and T_c (onset)] and specific-heat curves (denoted by T_s).

by firing a mixture of Nb_2O_5 and metallic Nb in a molar ratio of 1:3 in an evacuated fused-silica tube at 1100 °C for 72 h. The lithium content was determined by inductively coupled plasma spectroscopy. The as-prepared sample was slightly nonstoichiometric in lithium due to its volatility, $Li_{0.93}NbO_2$, which is very close to the values previously reported.[2,11,12] $Li_{0.68}NbO_2$ was prepared from $Li_{0.93}NbO_2$ by chemical treatments at room temperature using bromine or hydrochloric acid as an oxidative reagent. After the treatment, the sample changed from reddish to black, indicating that the electronic properties were modified. The powder x-ray-diffraction pattern showed that both the as-prepared and deintercalated samples are single phased with no trace of $LiNbO_3$ and Nb.

The low-temperature resistivity was determined by the standard four-point measurement with a Quantum Design physical property measurement system (PPMS). In the measurement, an alternating current of 200 μA, corresponding to a current density of about 5.33 mA/cm^2, was applied. The temperature dependence of the resistivity does not change by varying the measurement current from 100 to 500 μA. The low-temperature specific-heat measurements in the range from 0.5 to 7 K were performed with a ^{3}He heat-pulsed thermal relaxation calorimeter attached to the PPMS up to 3 T. The precision of the measurement is about 1%. The field dependence of thermometer and addenda was carefully calibrated before the specific heat was measured.

Figure 2 shows the temperature and field dependence of the resistivity for $Li_{0.68}NbO_2$. At zero field, the onset temperature of superconductivity is 5.5 K, and the resistivity becomes zero at about 4.8 K. The transition width is about 0.7 K. With increasing fields, the transition width is heavily broadened, similar as in high-T_c superconductors.[13–16] This broadening may result from the anisotropy of the upper critical field H_{c2}, arising from the two dimensionality of the material. Our polycrystalline sample consists of many randomly oriented crystallites. For each crystallite, H_{c2} takes its maximum when the applied field H is perpendicular to the c axis ($H \perp c$), and a minimum when $H \| c$. Thus the superconducting transition is broadened notably under an applied magnetic field since the superconductivity with minimal H_{c2} is first destroyed. The inhomogeneous distribution of charge carriers may also lead to the broadening of the transition width.

Figure 3 shows the temperature dependence of the upper critical field $H_{c2}(T)$ determined from the resistivity and specific-heat curves. The data denoted by T_0, T_{50}, T_{90}, and T_c (onset) represent the temperatures at which the resistivity equal to 0%, 50%, 90%, 100% of the normal-state resistivity, respectively. T_s is determined from the midpoint of the superconducting transition in the specific-heat curve and the error bar shows the one-half of transition width. The inset of Fig. 4 shows how T_s and the error bar are determined from the specific-heat data for $H=0.1$ T. The specific-heat jump is strongly suppressed at high field, thus only low-field T_s can be reliably determined. $H_{c2}(T)$ determined from the 90% normal-state resistivity agrees very well with that from the specific-heat measurement. Near T_c, H_{c2} shows a positive curvature. Similar positive curvature in $H_{C2}(T)$ was observed

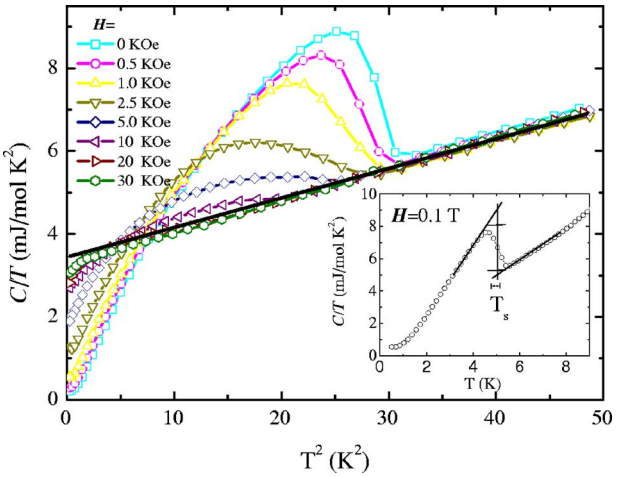

FIG. 4. (Color online) C/T vs T^2 at various applied fields for $Li_{0.68}NbO_2$. The solid line is a linear fit to the normal-state specific heat. The inset shows how T_s and the error bar is determined from the specific-heat data for $H=0.1$ T.

in high-T_c cuprates.[17,18] It may result from the fluctuation of the order parameter and the inhomogeneous distribution of charge carriers.

The specific-heat measurement is a powerful tool for investigating the low-lying superconducting quasiparticles. It probes bulk properties and can be used to determine the pairing symmetry of superconductors.[19–23] Figure 4 shows the measurement data of the specific heat for $Li_{0.68}NbO_2$. A clear anomaly associated with the superconducting transition is discerned at about $T \sim 5$ K at zero field. This anomaly persists with H up to 3 T. There is no upturn in all the curves of C/T down to 0.5 K. This suggests that the sample is free of magnetic impurities.

The measured specific heat C contains the contribution from both electrons and phonons, $C = C_{el} + C_{ph}$. At low temperatures, the phonon contribution to the specific heat C_{ph} does not depend on the applied magnetic field and follows the Debye law, i.e., $C_{ph} \sim T^3$, in both the normal and superconducting states. In the normal state, the electronic contribution to the specific heat C_{el} varies linearly with T, thus the total specific heat can be expressed as

$$C_n(T) = \gamma_n T + \alpha T^3, \tag{1}$$

where γ_n and α are temperature-independent coefficients. By fitting the normal-state data with this formula, we find that $\gamma_n = 3.588 \pm 0.038$ mJ/mol K^2 and $\alpha = 0.07258 \pm 0.000\,75$ mJ/mol K^4. This γ_n value is smaller than the corresponding value for Li_xNbS_2 (~ 10 mJ/mol K^2),[24] $NaCoO_2$ (~ 24 mJ/mol K^2),[25,26] $LiTi_2O_4$ (~ 19.15 mJ/mol K^2),[27] and Sr_2RuO_4 (~ 40 mJ/mol K^2).[28] The Debye temperature deduced from α is 462 ± 12 K.

The normal-state electronic specific-heat coefficient γ_n is proportional to the density of states of electrons at the Fermi level $N(E_F)$. In the free-electron model, it can be written as

$$\gamma_n = \frac{\pi^2}{3} k_B^2 N(E_F). \tag{2}$$

Novikov *et al.* calculated the band structure of $Li_{0.5}NbO_2$ using the full potential linear muffin-tin orbital (FLMTO) method.[8] They found that the density of states $N(E_F)$ at Fermi level is 6.02 1/eV. If we take this value for $Li_{0.68}NbO_2$, the value of calculated $\gamma_n \sim 3.85$ mJ/mol K^2 is close to 3.58 mJ/mol K^2, the value obtained from the specific-heat measurement. This signifies that the electron-phonon coupling is very weak in this material.

In the superconducting state, the electronic specific heat can be obtained by subtracting the phonon term from the total specific heat $C_{el} = C - C_{ph}$. As shown in Fig. 5(a), C_{el}/T drops with decreasing temperature. In the absence of magnetic field, C/T extrapolates to a small but finite value $\gamma_s = 0.195$ mJ/mol K^2 at zero temperature. This residual specific heat indicates that there is a residual density of states at the Fermi level, which in turn means that the superconducting volume fraction of the sample is less than 100%. From the ratio $(\gamma_n - \gamma_s)/\gamma_n$, we estimate the superconducting volume fraction of the sample to be 94.5%. This value of the superconducting volume fraction is rather high compared with the previous reports.[2,29] It is presumably due to the improved treatment of the sample quality.

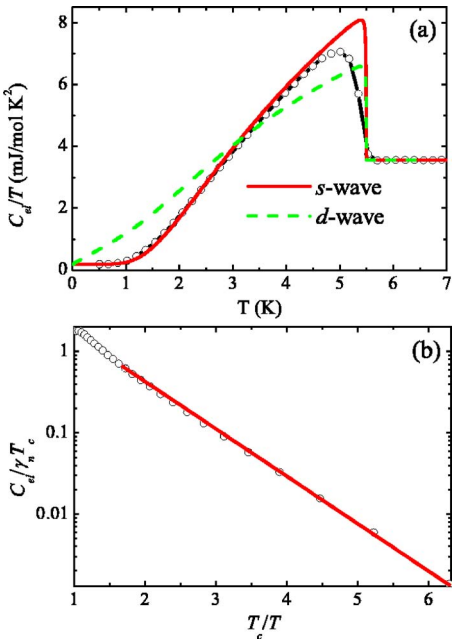

FIG. 5. (Color online) (a) C_{el}/T as a function of temperature for $Li_{0.68}NbO_2$. The solid and dashed lines are the theoretical curves for the BCS s- and d-wave superconductors, respectively. (b) $C_{el}/\gamma_n T_c$ vs T_c/T. The solid line is an exponential fit to the low-temperature data after subtracting the residual specific heat contributed from the normal volume fraction.

Figure 5(a) compares the measurement data with the BCS mean-field results of s- and d-wave superconductors. Apparently, the d-wave result deviate significantly from the experimental data in the whole temperature range. However, the s-wave result fits extremely well with the experimental data, especially in the low-temperature regime. The jump of the specific heat at T_c is less than the theoretical value. This is probably due to the fact that the superconducting transition of this material happens in a finite temperature range (0.7 K) rather than just at one point as in the BCS theory. By plotting C_{el} as a function of T_c/T in a semilogarithmic scale [Fig. 5(b)], we find that C_{el} indeed decreases exponentially with T at low temperatures. By further fitting the low-temperature data with the following formula:[30]

$$C_{el} \approx 2\sqrt{2\pi} k_B N(E_F) \Delta(0) \left(\frac{\Delta(0)}{k_B T} \right)^{3/2} e^{-\Delta(0)/k_B T}, \tag{3}$$

we find that $\Delta(0) \approx 0.8$ meV. This value of $\Delta(0)$ is close to that determined simply from T_c using the weak-coupling BCS formula $\Delta(0) = 1.76 k_B T_c = 0.76$ meV.

In conclusion, we have measured the field and temperature dependence of resistivity and specific heat of

$Li_{0.68}NbO_2$. The upper critical field is extracted from both the resistivity and the specific-heat curves. A notable specific-heat jump is observed at $T_c \sim 5.0$ K at zero field and suppressed by the applied field. By subtracting the phonon contribution, the electronic specific heat C_{el} is obtained from the measured data. The linear coefficient of C_{el} is found to be $\gamma_n = 3.588$ mJ/mol K^2 and the Debye temperature is $\Theta_D = 462$ K. Below T_c, C_{el} shows a thermal activated behavior and the temperature dependence of C_{el} agrees well with the BCS result for a *s*-wave superconductor.

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