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

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A high quality superconducting Li_{0.68}NbO_2 polycrystalline sample was synthesized 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 upper critical field \( H_{c2}(0) \) is estimated to be \( \sim 2.98 \) T. 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 of the BCS s-wave superconductors. 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_2·1.3H_2O [1] has stimulated great interest in the investigation of physical properties of quasi-two-dimensional materials with frustrations. Among them, lithium niobium oxide, LiNbO_2, has received considerable attention since superconductivity was discovered upon partial deintercalation of lithium atoms in this material [2]. This compound is of certain characteristics of high-\( T_c \) cuprates. There exists a strong hybridization of Nb 4d states with O 2p states, and an elevated density of oxygen states at the \( E_F \) [3, 4]. Since many layered oxides, including high-\( T_c \) cuprates, Sr_2RuO_4, and Na_{0.3}CoO_2·1.3H_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_{2}NbO_2 has a layered structure analogous to MoS_2. Along the c-axis, the lithium planes and NbO_6 trigonal-prismatic layers are stacked alternatively [5]. 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 4d energy levels split into a pattern with \( d_{xz} < d_{z^2} < d_{xy} < d_{zx} < d_{yz} \) [6]. 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, 8, 9]. So it exhibits semiconducting behavior in low temperatures. However, in Li_{2}NbO_2 with partial removal of lithium, the conduction band that contain holes is formed [7]. The metallic behavior is observed and superconductivity occurs with \( T_c \) of \( \sim 5 \) K.

The burgundy-red polycrystalline LiNbO_2 was prepared by heating Li_{3}NbO_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.
and NbO was prepared by firing a mixture of Nb$_2$CO$_3$ and Nb$_2$O$_5$ in a molar ratio of 3:1 at 900°C in air for 48 h, and NbO was prepared by firing a mixture of Nb$_2$O$_5$ and metallic Nb in a molar ratio 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 non-stoichiometric in lithium due to its volatility, Li$_{0.68}$NbO$_2$, which is the same as previous reports [2, 10, 11]. 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 oxidative reagent. After the treatment, the sample changed to reddish to black, indicating that the electronic properties were modified. Powder x-ray diffraction pattern obtained by a M18AHF x-ray diffractometer using CuK$_\alpha$ radiation showed that both the as-prepared and deintercalated samples are single phased with no trace of LiNbO$_2$ and Nb.

The low temperature resistivity was determined by the standard four point measurement with a Quantum Design PPMS. 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 Tesla. 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, a superconducting transition begins at 5.5 K, and the resistivity becomes zero at about 4.8 K. The transition width is about 0.7 K.

In Fig. 3, the temperature dependence of the upper critical field $H_{c2}(T)$, determined from the temperature at which the resistivity is equal to 90% of its normal state value for a given field, is shown. From the Ginzburg-Landau theory, it is known that $H_{c2}$ is inversely proportional to the square of the coherence length $\xi$:

$$H_{c2} = \frac{\Phi_0}{2\pi \xi^2},$$

$$\xi^2 = \frac{\hbar^2}{2m^*\alpha(T)},$$

where $\Phi_0$ is the flux quanta, $\alpha(T) \propto (1-t^2)/(1+t^2)$ and $t=T/T_c$ is the reduced temperature. Therefore, $H_{c2}(T)$ can be expressed as:

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

By fitting the experimental data with the above equation (solid curve in Fig. 3), we find that the zero temperature upper critical field $H_{c2}(0) \approx 2.98$ T. The coherence length $\xi_{c2}(0)$ estimated from this value of $H_{c2}(0)$ is $\sim 106$ Å, which is very close to the coherence length of Na$_{0.3}$CoO$_2$-1.3H$_2$O (100 Å). [12, 15]

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 [16, 17, 18, 19, 20]. 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, $C = C_{el} + C_{ph}$. In 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 $C_{el}$
from the total specific heat can be obtained by subtracting the phonon term. The electron-phonon coupling is very weak in this material. This signifies that the residual specific heat contributed from the normal volume fraction.

\[ C_n(T) = \gamma_n T + \alpha T^3. \]  

(4)

where \( \gamma_n \) and \( \alpha \) are temperature independent coefficients. By fitting the normal state data with this formula, we find that \( \gamma_n = 3.588 \pm 0.038 \text{ mJ/mol K}^2 \) and \( \alpha = 0.07258 \pm 0.00075 \text{ mJ/mol K}^4 \). This \( \gamma_n \) value is smaller than the corresponding value for Li\(_2\)NbS\(_2\) \( (\sim 10 \text{ mJ/mol K}^2) \) \cite{23}, NaCoO\(_2\) \( (\sim 24 \text{ mJ/mol K}^2) \) \cite{22, 23}, Li\(_2\)Ti\(_2\)O\(_4\) \( (\sim 19.15 \text{ mJ/mol K}^2) \) \cite{24} and Sr\(_2\)RuO\(_4\) \( (\sim 40 \text{ mJ/mol K}^2) \) \cite{23}. The Debye temperature deduced from \( \alpha \) is 462 ± 12K.

The normal state electronic specific heat coefficient \( \gamma_n \) is proportional to the density of states of electrons at the Fermi level \( N(E_F) \). In the free electron gas model, it can be expressed,

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

(5)

Novikov et. al calculated band structure of Li\(_{0.68}\)NbO\(_2\) using the full potential linear-muffin-tin-orbital (FLMTO) method.\cite{7} They found 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 \( \gamma_n \sim 3.85 \text{ mJ/mol K}^2 \) 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 \( \gamma_s = \text{0.195 mJ/mol K}^2 \) 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.\cite{2, 26} It is presumably due to the improved treatment of the sample quality.

Figure 5(a) compares the measurement data with the BCS mean-field results of s- and d-wave superconductors. Apparently, the d-wave result deviates 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 semi-logarithmic scale (Figure 5(b)), we find that \( C_{el} \) indeed decreases exponentially with \( T \) in low temperatures. By further fitting...
the low temperature data with the formula

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

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

In conclusion, we have measured the field and temperature dependence of resistivity and specific heat of Li_{0.68}NbO_2. From the resistivity data, the upper critical field is deduced and analyzed using the Ginzberg-Landau theory. A notable specific heat jump is observed at \( T_c \approx 5.0 \text{ K} \) 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 \( \gamma_n = 3.588 \text{ mJ/mol K}^2 \) and the Debye temperature is \( \Theta_D = 462 \text{ K} \). 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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