Anomalous magnetoresistance in the spinel superconductor LiTi$_2$O$_4$

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LiTi$_2$O$_4$ is a unique compound in that it is the only known spinel oxide superconductor. The lack of high quality single crystals has thus far prevented systematic investigations of its transport properties. Here we report a careful study of transport and tunnelling spectroscopy in epitaxial LiTi$_2$O$_4$ thin films. An unusual magnetoresistance is observed which changes from nearly isotropic negative to prominently anisotropic positive as the temperature is decreased. We present evidence that shows that the negative magnetoresistance likely stems from the suppression of local spin fluctuations or spin-orbit scattering centres. The positive magnetoresistance suggests the presence of an orbital-related state, also supported by the fact that the superconducting energy gap decreases as a quadratic function of magnetic field. These observations indicate that the spin-orbital fluctuations play an important role in LiTi$_2$O$_4$ in a manner similar to high-temperature superconductors.
L demand. LTO (LiTl2O4) is an oxide superconductor with a spinel crystal structure. It was discovered in early 1970’s by Johnston et al., and it has the superconducting transition temperature $T_c$ of 11 K (ref. 1). Although its $T_c$ can be described by band-structure calculations using the McMillan formula with a weak electron-phonon coupling constant ($\lambda_{el-ph} \approx 0.6$; refs 3, 4), an enhanced density of states or an equivalently larger coupling constant has been unveiled from specific-heat$^{5,6}$ and magnetic susceptibility measurements$^7$. Other measurements like nuclear magnetic resonance$^8$, point contact Andreev reflection spectroscopy$^9$, and resonant inelastic soft-x-ray scattering$^{10}$ have revealed the significance of $d$-$d$ electron correlations. It is naturally expected that the correlations play a role in the microscopic mechanism for its superconductivity.

Moreover, in contrast to perovskite oxides, LTO has a cubic symmetry with the space group of $Fd\overline{3}m$, where the lithium and titanium cations are located at the tetrahedral $8a$ and octahedral $16d$ sites, respectively. On one hand, the $t_{2g}$ sub-band of Ti is in high degree of degeneracy, remaining in a narrow $d$-band metal with significant electron–electron interaction$^8$. On the other hand, the Ti sublattice, in mixed valences of Ti$^{3+}$ and Ti$^{4+}$, is frustrated and favours short-range spin ordering$^{12}$. Therefore, it is interesting to see whether spin-orbital fluctuations also play a role in superconductivity in LTO, akin to the perovskite-type high $T_c$ superconductors$^{13,14}$. However, the development of an understanding of this system has been hampered by the lack of sample reproducibility and the availability of single crystals or high quality thin films$^{1,7,15}$. Recently, high quality epitaxial LTO thin films were successfully grown by pulsed laser deposition$^{16,17}$, thus opening the door for systematic experiments on LTO.

In this paper, we present results of transport and tunnelling studies on single crystalline-like epitaxial LTO thin films. The suppression of the superconducting energy gap as a quadratic function of magnetic field, and an anomalous crossover of magneto resistance from prominently anisotropic positive to nearly isotropic negative with increasing temperature have been observed for the first time. In addition to the extracted key parameters from the combined tunnelling and transport measurements, a full picture of LTO has emerged: the data suggest the presence of spin-orbit scattering/spin fluctuations below ~100 ± 10 K and an orbital-related state below $T_{ch}$ ~50 ± 10 K. We propose a theoretical model to account for the relation between the superconducting energy gap and the magnetic field.

Results
Charge transport data and tunnelling spectra. The (001)-Oriented LTO thin films were epitaxially grown on (001)-oriented MgAl2O4 substrates by pulsed laser deposition. Our LTO films consistently display $T_c$ of 11 ± 0.25 K with narrow transition widths of <0.5 K. We have found that different films have different residual resistivity ratios (RRR). The films were patterned into Hall bars to carry out Hall and normal resistivity measurements. Tunnelling spectroscopy was performed where Pt–Ir tips were used to make point contacts in the out-of-plane axis direction (c-axis, perpendicular to the film plane) of LTO$^{18}$.

Figure 1a shows the resistivity versus temperature curves for samples with two different RRR ratios: 6.25 and 3 for samples L1 and L2, respectively. L1 and L2 have similar resistivity values at room temperature and the same $T_c$. The normal state resistivity of both samples can be fitted to a curve consistent with the Fermi liquid behaviour, $\rho = \rho_0 + AT^2$ (grey lines) from 40 to 120 K with residual resistivity ($\rho_0$) of ≈71 μΩ cm for L1 and ≈166 μΩ cm for L2. The deviation from the Fermi liquid behaviour at low temperatures is caused by an enhanced electron–electron

![Figure 1 | Resistivity and Hall behavior of LiTl2O4 thin films.](image-url)
interaction as discussed below. By sweeping the magnetic field perpendicular to the film surface ($B \perp$ in-plane (ab plane)) at fixed temperatures, the Hall resistivity, that is, $\rho_{xy} = \frac{e}{2}\frac{V_y}{I}$, has been extracted. $\rho_{xy}$ data for different temperatures are plotted in Fig. 1b, where $V_y$ is the Hall voltage obtained by subtracting the transverse voltage in negative field from that in positive field, and $t$ is the thickness of the film. In the normal state, the Hall resistivity is always proportional to the magnetic field, positive and temperature independent, strongly suggesting the presence of one type of charge carriers (holes) and a simple electronic band structure. The charge carrier concentration is calculated assuming a parabolic band structure, that is, the Hall coefficient $R_h(=\frac{1}{e^2}\frac{I}{V_y})$ and $L_2$ have almost the same hole concentration of $\sim 3 \times 10^{22}$ cm$^{-3}$ (Fig. 1c), indicating that the different RRRs are likely caused by the difference in mobility values.

The point contact measurements were carried out on L1 before it was patterned into a Hall bar for transport measurements. As described by the Blonder, Tinkham and Klapwijk (BTK) model, the tunnelling regime is achieved for $Z > 1$, where $Z$ represents the tunnelling barrier height and the Fermi velocity mismatch. The differential conductance spectrum shows a clear temperature and field-dependent coherence peak. The normalized differential conductance spectra with and without applied magnetic field are shown in Fig. 2a–c as a function of bias voltage (see Supplementary Note 1 for normalization procedure). The normalized experimental curves were fitted using a modified BTK model with a complex energy $E = E + i\Gamma$ (ref. 21). The broadening $\Gamma$ term, which takes into account sample in-homogeneity and a finite quasi-particle lifetime by scattering, is temperature independent in zero field, but application of magnetic field has been found to lead to an additional pair-breaking factor, which in effect is akin to an enhanced $\Gamma$ (ref. 23).

Fitting parameters and superconducting energy gap. Several key points can be made from the fitting of our tunnelling spectra. First, the Z value of our Pt–Ir/LTO junction is $\sim 2.4$, which is independent of temperature and field. Second, zero-field spectra give a constant $\Gamma_0$ of $\sim 0.94$ meV (Supplementary Fig. 2), but data in field have to be fitted with an increasing $\Gamma$ as the field is increased (Supplementary Fig. 3). Third, the temperature dependence of the superconducting energy gap can be fitted well with the BCS theory (Fig. 2d), and the observed $2\Delta_0/k_BT_c = 4$ ($\Delta_0 = 1.93$ meV) is consistent with previous reports, indicating that LTO is a medium-coupling BCS superconductor. Moreover, a simple relation of $\Delta(B, T) = \Delta_0(T)(T^2 - B^2/2C_0)$, can be used to scale the field-dependent energy gap at different temperatures, for example, $T = 2, 6, 10$ K (Fig. 2e). Accordingly, $B_{c2}$ can be extracted from the point contact spectra with $B_{c2}(2K) \sim 16T$.

We also employed a two-channel method derived from the BTK model to fit our experimental data. In this method, the pairing effect by field is considered as a normal channel (N) superposed onto the superconducting channel (S). Assuming the differential conductance to take the form $G(h) = G_N(1 + (1 - h^2)G_S)$ with $h = B/B_{c2}$, the normalized differential conductance in field should obey the polynomial form $G_G(x) = \frac{G}{G_0} = h^2 + (1 - h^2)\frac{G_0}{G_0}$, where $G_0$ is obtained from the BTK model with a constant $\Gamma$. The best fitting requires $r = 2$. We note that this value is consistent with those used to fit data for point contacts with other superconductors such as Nb, Mo/Sb$_2$ and Dy$_{1.08}$Y$_{0.92}$Rh$_2$B$_4$ (ref. 24). In this case, the relation, $\Delta(B) \sim \Delta B^2$ emerges again, and the $\Delta$ values extracted from the two fitting methods are similar (Fig. 2e). To the best of our knowledge, none of the existing theoretical models can account for the quadratic relation. When $B$ is close to $B_{c2}$, the Maki formula can be analytically expressed as $[\Delta(0)]^2 \sim \frac{\rho_{xy}}{\rho_{xy}^0}$, where $\Delta$ represents the averaged energy gap taking into account the effect of vortices, and $\rho_{xy}$ is the first derivative of the digamma function with $A$ the pair-breaking parameter proportional to $B$ when $B \perp ab$ plane, but this does not lead to a quadratic field dependence of the superconducting energy gap.

Theoretical model. We note, however, that if there exists an additional anisotropy axis, which breaks the intrinsic symmetry of the system, for example, orbital ordering or a background nematicity, $\Delta(B) \sim B^2$ can arise. To simplify the discussion without loss of generality, we assume that the superconducting order parameter is a three-component vector, $\Delta = (\Delta_x, \Delta_y, \Delta_z)$. The isotropic gap is then equal to the modulus of this vector: $\Delta_0 = (\sum \Delta^2)^{1/2} = (\Delta_x^2 + \Delta_y^2 + \Delta_z^2)^{1/2}$. In zero field, the orientation of the local spin of the Cooper pair changes in real space, while the value of the gap does not change. Therefore, the average magnetic moment of Cooper pairs vanishes, that is, $\langle \chi(r) \rangle = 0$. However, in magnetic field $B$, the magnetic moments of Cooper pairs can be partially polarized, and therefore the susceptibility $\chi$ can develop a paramagnetic component. Thus, we have $\chi_{para} = \chi_{para} + \chi_{dia}$. The last term is the conventional diamagnetic susceptibility of a superconductor.

The first term $\chi_{para}$ should be a function of the magnetic moments of the Cooper pairs, which contributes to the symmetry invariants. There are in general three symmetry invariants here. The first one is just $\Delta \Delta$, the second one is $\Delta \Delta$. The additional anisotropy axis, for example, orbital ordering or background nematicity associated with some vector $b$ results in another invariant as $\Delta b$. In the vicinity of the phase transition, we can use the Taylor expansion to obtain:

$$\chi_{para}(\Delta B, b, \Delta B/\Delta b) = \chi_{para}(0, 0, 0) + \chi_{para}(0, 0, \Delta B)$$

$$+ \chi_{para}(0, 0, 0) + \Delta B + \cdots$$

In using this expression, the total free energy of the superconductor in the lowest order with superconducting order parameter can be written in the form:

$$F(\Delta) = \frac{1}{2} (\Delta \Delta) + 2\delta (\Delta B/\Delta B) + \mu (\Delta B) + \cdots$$

Minimization of the free energy with respect to $\Delta$ will give the expression $\Delta(B) = (\sum \Delta^2)^{1/2} = (\Delta_0^2 - 4\delta B^2/2C_0)^{1/2}$ where $\Delta_0$ and $\delta$ are the parameters of the Ginzburg–Landau expansion, and $b$ is the modulus of the vector $b$ (See Supplementary Note 4 for details). This represents the first plausible explanation giving rise to the relation, $\Delta(B) \sim B^2$. As for the origin of the symmetry breaking, which gives rise to the vector $b$ in LTO, we propose that there is an onset of orbital ordering, which takes place in LTO below a transition temperature $T_{orb}$, arising from orbital degeneracy of t$_{2g}$ sub-band.

We would like to point out that although this relation has not been carefully examined previously, we also observe it in some cuprates, namely, electron-doped (Nd, Ce)$_2$CuO$_4$ and (Pr, La, Ce)$_2$CuO$_4$ (Supplementary Fig. 4), indicating the presence of a similar symmetry breaking ordering in these compounds. We believe other ordering mechanisms such as spin stripes or charge density wave may also lead to a symmetry breaking resulting in the vector $b$. The electronic nematicity has been widely discussed in hole-doped cuprates and Fe-based superconductors, as a competing order to the superconductivity. The exact nature of the ordering in electron-doped cuprates is beyond the scope of the present work, but the discovered quadratic relation is perhaps not uncommon across different types of superconductors. On the
other hand, we note that the relation from the Maki formula is observed in superconductors without symmetry breaking, for example, \( \Delta^2(B) \sim -B \) or \( -B^2 \) for \( \text{Zn} \) (ref. 34) and \( \Delta^2(B) \sim -B \) for \( \text{Ba,K} \)BiO\(_3\) (ref. 35). It would therefore be of broad interest to investigate the possibility of occurrence of the quadratic relation in other superconductors also: it can possibly serve as a signature underpinning different mechanisms leading to intrinsic symmetry breaking, which results in the presence of an additional anisotropy axis.

Zero bias conductance. The normalized zero bias conductance (ZBC) at 2 and 6 K shows a linear dependence on the magnetic field (Fig. 2f). Such a relation has been reported in systems such as \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8 \) and \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \) overdoped with intercalating \( \text{HgBr}_2 \) molecules\(^{36}\) and in nanosized Pb islands on a silicon wafer\(^{37}\).

The departure from linearity in-field-dependent ZBC has previously been observed in MgB\(_2\) (ref. 38) and YNi\(_2\)B\(_2\)C (ref. 39), associated with the fact that they are multiband superconductors. In the Ca\(_{0.05}\)Na\(_{0.2}\)Cu\(_2\)O\(_2\)Cl\(_2\) \((x = 0.14)\), the field dependence scales as \( B \log B \), suggested to be an indication of a dirty \( d \)-wave superconductor\(^{40}\). Previous specific heat experiments have suggested that LTO is an \( s \)-wave superconductor\(^{6}\). Thus, based on the lack of departure from the linearly dependent ZBC, we conclude that LTO is not likely to be a multiband superconductor.

Calculated key physical quantities. Combining the transport and tunnelling data, we were able to extract key parameters for LTO. The Ginzburg–Landau coherence length, the size of the vortex core in type II superconductor is estimated to be \( \zeta_{GL} = (\frac{\Phi_0}{2\pi E_F})^{1/2} = 4.47 \) nm. The mean free path of \( l = 1.8 \) nm is

### Table 1 | Comparison of physical parameters of LiTi\(_2\)O\(_4\) to values from previous work.

|          | \( T_c \) (K) | \( \Delta \) (meV) | \( \zeta_{BCS} \) (nm) | \( \zeta_{GL} \) (nm) | \( n \) \( \text{cm}^{-2} \) | \( m^* / m_0 \) | \( l \) (nm) | \( v_F \) \( \text{m s}^{-1} \) | \( N(E_F) \) |
|----------|--------------|-------------------|------------------------|------------------------|-------------------------|----------------|-------------|-----------------|-----------------|
| Present  | 11 ± 0.25    | 1.93 ± 0.01       | 14.9                   | 4.47                   | 3 \times 10^{22}        | 8.11            | 1.84        | 1.37 \times 10^5 | 0.96            |
| Previous | 11.5 ± 0.5   | 1.9               | —                      | 4.1-4.6                | 1.35 \times 10^{22}     | 9.4             | 3.2         | —               | 0.97            |

The quantities in the present work were obtained from transport and tunnelling results on Sample L1. Since most of the earlier studies were carried out on polycrystalline samples, the parameters such as carrier density \( n \), effective mass \( m^* \), and density of states \( N(E_F) \) are from previous magnetic susceptibility measurements using nearly free electron approximations\(^{2}\). The mean free path \( l \) was calculated from the specific heat data\(^{6}\). We compare the Ginzburg–Landau coherence length \( \zeta_{GL} \) to the value reported by another thin film study\(^{16}\), and the superconducting energy gap \( \Delta \) to the value obtained from an Andreev study on polycrystalline samples\(^{8}\).
deduced from the Drude model $\rho_0 = \frac{h v_f}{ne^2}$, where the Fermi wave vector $k_F = (3\pi^2 n)^{1/3} = 0.96 \text{ Å}^{-1}$. Since $l < \xi_{\text{GL}}$, the BCS coherence length of $\xi_{\text{BCS}} = 14.9 \text{ nm}$ is calculated from the dirty limit relation, $\xi_{\text{GL}} = \frac{0.855 \xi_{\text{BCS}}}{(1 - x)^{1/2}}$. We then calculate the Fermi velocity from the formula, $v_F = \frac{\hbar v_f}{\pi \Delta}$, and arrive at an effective mass of $m^* = 8.11$ (with $m_0$ being the free electron mass), and the density of states at the Fermi level is found to be $N(E_F) = 0.96$ states per eV atom.

We compared these parameters to those obtained from previous reports on LTO. Only $T_c$, and $\xi_{\text{GL}}$ values have been previously reported on thin films, and the other quantities were from the magnetic susceptibility, Andreev reflection and specific heat measurements on polycrystalline samples. As seen in Table 1, the values obtained in the present work are consistent with those from previous reports. We note that in polycrystalline samples, the grain boundaries prevent accurate calculations from the transport measurements due to boundary scattering, but the parameters could be extracted from heat capacity and susceptibility data. These values indicate that the nearly free electron model can capture the main physics of the LTO system.

**Field direction dependence of magnetoresistivity.** In the normal state, we observe an anomalous MR behaviour. Figure 3a illustrates the field-dependent MR in sample L1 when $B \perp ab$ plane. The MR gradually decreases from positive to negative with increasing temperature, and a crossover is observed at $50 \pm 10 \text{ K}$. In the inset of Fig. 3a, the MR is plotted as $B^2$. The positive MR is proportional to $B^2$, whereas the negative MR is not. In the case of $B \parallel ab$ plane, both orbital and spin effects can contribute to MR, and in order to discern the different contributions additional measurements were carried out where the field was also applied in the film plane with $B/|I|$ (parallel to current) and $B \perp I$ (normal to current). In Fig. 3b, the temperature dependence of MR is plotted for both L1 (grey symbols) and L2 (red symbols). The negative MR is nearly independent of the field directions, but the positive MR displays unambiguous anisotropy, that is, MR $(B \perp ab)$ plane $> MR (B//ab$ plane, $B \perp I) > MR (B//ab$ plane$/I)$. Moreover, the MR changes its sign when $B//I$, as seen in Fig. 4a. The first derivative of $\rho_{xx}(T)$ in zero field (symbols) starts to deviate from the Fermi liquid behaviour $(d\rho_{xx}/dT \sim T)$ at roughly the same range of temperature as seen in Fig. 4b, indicating the presence of an enhanced electron–electron interaction.

Such transport data collectively point to the presence of a phase transition or crossover with a characteristic temperature $T_{ch}$ of $\sim 50 \pm 10 \text{ K}$. As discussed above, we believe orbital ordering results in the relation, $\Delta(B) \sim B^2$. Thus, we associate $T_{ch}$ with the onset of an orbital-related state such as orbital ordering or nematicity (see Supplementary Note 4). If the LTO system indeed has such a symmetry breaking feature, it should also manifest itself in the anisotropy of the in-plane angular-dependent magnetoresistivity (AMR) measurements, and a twofold symmetry would be expected, similar to the case of iron arsenide superconductors. We indeed observe a twofold AMR in LTO (Fig. 4c). Note that a strong enhancement in amplitude of the twofold symmetry takes place below $T_{ch}$; we associate this with the orbital-related ordering. On the other hand, we find that the starting temperature of the twofold AMR is $\sim 100 \pm 10 \text{ K}$, far above the $T_{ch}$.

**Temperature dependence of magnetic susceptibility.** To understand this unusual behaviour, we also measured the temperature-dependent susceptibility in zero field and field cooling. The $\chi(T)$ in zero-field cooling data shows a clear screening effect due to superconductivity at $11 \text{ K}$ (Fig. 4e). In-field cooling, we find that the residual susceptibility, $\delta\chi(T)$, found by subtracting a paramagnetic component from the $\chi(T)$, starts to increase below $100 \pm 10 \text{ K}$ (Fig. 4d), corresponding to the same temperature where the twofold symmetry emerges. The amplitude of the twofold symmetry exhibits an abrupt increase at $T_{ch} = 50 \pm 10 \text{ K}$. We, thus, attribute the twofold AMR to two sources: one related to a spin interaction starting at a higher temperature ($100 \pm 10 \text{ K}$), and the other associated with an orbital effect (discussed below) becoming pronounced below $T_{ch} = 50 \pm 10 \text{ K}$.

**Discussion**

Our findings, thus far, can be summarized in the following three points: (1) With decreasing temperature, the magnetic susceptibility increases and deviates from the Curie–Weiss behaviour at $< 100 \pm 10 \text{ K}$, while the in-plane AMR starts to show a twofold symmetry and the magnetoresistivity is negative in field; (2) At $T_{ch} \sim 50 \pm 10 \text{ K}$, the sign of magnetoresistivity changes to positive and the twofold symmetry becomes more prominent, where we also observe deviation from the Fermi liquid behaviour; (3) Below $11 \text{ K}$, LTO enters the superconducting state, where the superconducting energy gap decreases as a function of $B^2$.

![Figure 3](naturecommunications/images/figure3.png)

**Figure 3 | Temperature dependence of magnetoresistivity.** (a) The transverse magnetoresistivity with $B \perp ab$ plane, $\Delta \rho_{xx} = \rho_{xx}(B) - \rho_{xx}(0T)$, changes from negative to positive as temperature is decreased. The crossover temperature is $\sim 50 \pm 10 \text{ K}$. The positive magnetoresistivity is proportional to $B^2$ as seen in the inset, whereas the negative MR is not. (b) Magnetoresistivity at $7 \text{ T}$ plotted against the temperature. The dark and red symbols are for samples L1 and L2, respectively. The magnetic field was applied along three different directions, that is, $B//ab$ plane ($B//I$, $B \perp I$) and $B \perp ab$ plane. The error bars are maximum data noise in determining the magnetoresistivity. The negative magnetoresistivity is nearly isotropic, whereas the positive magnetoresistivity shows unambiguous anisotropy.

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Generally, MR can result from charge, orbital or spin interactions, as well as interactions among them\(^\text{42}\). The observed constant Hall coefficient and smooth temperature evolution of the \(c\)-axis lattice parameter (Supplementary Fig. 8) preclude the presence of charge density waves, which normally influences the Hall coefficient\(^\text{42}\). The mean free path of the ‘clean’ sample (LI) is 1.84 nm in the zero-temperature limit, which is only about two unit cells of the LTO lattice. Therefore, a grain boundary effect is unlikely to have a dominant role in the MR behaviour. The combination of points (2) and (3) above supports an orbital effect as the origin of the positive anisotropic MR below 50 ± 10 K, which introduces the additional anisotropic MR below 100 ± 10 K, coincident with the starting temperature of the twofold symmetry of in-plane resistivity. (e) The susceptibility with zero-field cooling shows a good superconducting screening signal, suggesting our LTO films are of high quality. The shading areas around 100 K and 50 K represent the uncertainties in defining the starting point of the anisotropic AMR and the abrupt increase, respectively.

We note that in \(\text{La}_{2-x}\text{Ce}_x\text{CuO}_4\) thin films, antiferromagnetism (AFM) has been identified as the main cause of a twofold symmetry of AMR and a negative MR\(^\text{44}\), while in Fe-based superconductors the anisotropy of in-plane charge transport was accompanied by a discontinuous jump in MR. This is in contrast to the observation in LTO, where there is no discontinuous jump. Moreover, the LTO system has a frustrated Ti sublattice structure is different from the perovskite one, we believe it is not unreasonable to link the appearance of a twofold symmetry of AMR at 100 ± 10 K to local AFM spin correlations, and the sudden enhancement at 50 ± 10 K to an orbital related state.

In antiferromagnetic metals, a sign change in MR is expected theoretically at the Neel temperature due to the \(s\)-\(d\) electron interaction\(^\text{45}\). However, this idea is based on long range AFM, and the change in sign from negative to positive is to be accompanied by a discontinuous jump in MR. This is in contrast to the observation in LTO, where there is no discontinuous jump. Moreover, the LTO system has a frustrated Ti sublattice containing equal numbers of \(\text{Tl}^{3+}\) and \(\text{Tl}^{4+}\), and thus a long range AFM ordering is unfavourable\(^\text{12}\). The emergence of...
short-range AFM ordering has been reported in V-doped LTO by nuclear magnetic resonance and in LiV$_2$O$_4$ by inelastic neutron scattering. Note that the AMR measurements cannot be used to tell whether the AFM is static or dynamic. It is possible that local spin fluctuations are responsible for the negative MR. We consider an alternative explanation due to the effect of spin-orbit coupling. When the orbital ordered (nematic) state is destroyed at $T > T_{chn}$, some ‘fluctuating’ islands may have a finite lifetime and serve as additional (magnetic) scattering centres for the electron transport. When the magnetic field is applied, some of these islands disappear and the resistivity decreases. This is exemplified in thin metallic Mg films covered with small controlled quantities of a magnetic ion such as Fe or a heavy ion with large spin-orbit coupling such as Au: the magnetoresistance changes its sign from negative to positive on experiencing an increase in the number of spin-orbit scattering centres. Perhaps a similar mechanism is at work in LTO.

In conclusion, detailed properties of superconducting LTO were investigated for the first time in high quality thin films. Many properties are consistent with previous work on polycrystalline samples. We observe one type of charge carrier and a $\Delta T_c$ value consistent with a medium-coupling BCS superconductor. The main physics can be captured by the nearly free electron model. However, we find two new and distinct features in this system. In the superconducting state, a scaling law, $\Delta(B) \sim -B^2$ at $T < T_c$, is extracted from our point contact spectra. This behaviour had not been predicted by any previous theory. In the normal state, an anomalous MR, which crosses over from nearly isotropic negative MR to an anisotropic positive MR with decreasing temperature, is observed. The anisotropic positive MR likely originates from the enhanced electron–electron interaction due to the orbital related ordering below $T_{chn} \approx 50 \pm 10$ K. The negative MR occurring at $100 \pm 10$ K possibly stems from the suppression of spin-orbit scattering or local spin fluctuations. We present a new theoretical model based on the proposal that there is orbital ordering in the superconducting state to account for the relation $\Delta(B) \sim -B^2$. The fact that this relation is also observed in other materials ($\text{Nd}_x\text{Ce}_{1-x}\text{CuO}_4$ and ($\text{Pr}_x\text{La}_{1-x}\text{Ce}_x\text{CuO}_4$)) points to the broader fact that this relation is also observed in other materials under varying interactions and different types of superconductors.

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Author contributions

K.J., R.L.G. and I.T. designed the research; S.M., S.Y., R.S. and J.S. prepared the thin films; K.J. performed transport and point contact measurements; X.Z., Y.J., H.S.Y. and J.Y. complemented transport measurements; K.J., G.H., L.S., F.V.K. and R.L.G. analysed the data; K.J., R.L.G. and I.T. wrote the paper.

Additional information

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