$^{77}$Se and $^{63}$Cu NMR studies of the electronic correlations in Cu$_x$TiSe$_2$ ($x = 0.05$, 0.07)

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Received 23 February 2010, in final form 3 June 2010
Published 28 June 2010
Online at stacks.iop.org/JPhysCM/22/295601

Abstract

We report a $^{77}$Se and $^{63}$Cu nuclear magnetic resonance (NMR) investigation on the charge-density-wave (CDW) superconductor Cu$_x$TiSe$_2$ ($x = 0.05$ and 0.07). At high magnetic fields where superconductivity is suppressed, the temperature dependence of $^{77}$Se and $^{63}$Cu spin–lattice relaxation rates $1/T_1$ follow a linear relation. The slope of $^{77}$Se $1/T_1$ versus $T$ increases with the Cu doping. This can be described by a modified Korringa relation which suggests the significance of electronic correlations and the Se 4p- and Ti 3d-band contribution to the density of states at the Fermi level in the studied compounds.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One of the central issues in condensed matter physics is to understand the interplay between diverse competing phases: for example, antiferromagnetism and superconductivity in the high-$T_c$ cuprates [1] and charge-density-wave (CDW) order and superconductivity in transition metal dichalcogenides [2]. Very recently, the CDW compound TiSe$_2$ was successfully doped by a Cu intercalation between adjacent layers [3]. This allows for tuning the electronic properties of Cu$_x$TiSe$_2$ by controlling the Cu concentration $x$. The Cu doping drives the system to a superconducting state around $x = 0.04$. In this regard, the Cu$_x$TiSe$_2$ system provides a unique opportunity to study the competition between the CDW and superconducting phases in a controlled way.

The Cu$_x$TiSe$_2$ compound has a layered structure with trigonal symmetry where the Ti atoms are in octahedral coordination with Se. The Cu atoms occupy the positions between the TiSe$_2$ layers which leads to an expansion of the lattice parameters [3]. The parent compound TiSe$_2$ is one of the first CDW compounds, where a commensurate CDW at $T_{cdw} \sim 200$ K with a wavevector $Q = (2a, 2a, 2c)$ was reported [2, 4]. The CDW transition is not driven by the nesting of a Fermi surface. Instead it is either due to a transition from a small indirect gap into a larger gap state with a slightly different location in the Brillouin zone or due to a particle–hole symmetry [3, 5]. The CDW transition in TiSe$_2$ can be suppressed continuously by a Cu doping while superconductivity emerges with a maximum $T_c = 4.15$ K at $x = 0.08$. The electronic structure has been investigated by band structure calculations and ARPES measurements [5–8]. The remarkable feature is that the CDW order parameter competes microscopically with superconductivity in the same band and that the parent compound TiSe$_2$ is a correlated semiconductor and the Cu doping enhances the density of states and raises the chemical potential.

Various measurements were also performed to further investigate the role of the Cu doping [9–13]. Thermal
conductivity suggests that this system exhibits conventional s-wave superconductivity due to the absence of a residual linear term $\frac{\partial \sigma}{\partial T}$ at very low temperatures [9]. The weak magnetic field dependence of thermal conductivity indicates a single gap that is uniform across the Fermi surface. Furthermore, it is suggested that the 4p Se band is below the Fermi level and superconductivity is induced because of the Cu doping into the 3d Ti bands [9]. An optical spectroscopy investigation on Cu$_{0.07}$TiSe$_2$ reveals that the compound has a low carrier density and has an anomalously metallic state because of the substantial shift of the screened plasma frequency [10]. This is corroborated by the temperature-independent Hall coefficient $R_H$ observed in heavily Cu-doped samples [11]. Raman scattering measurements as a function of doping suggest that the $x$-dependent mode softening is associated with the reduction of electron–phonon couplings and the presence of a quantum critical point within the superconducting region [12].

In this paper we address the issue of electronic correlations in this system as a function of Cu doping using $^{77}$Se and $^{63}$Cu NMR. We studied two doping levels of Cu$_x$TiSe$_2$ which exhibit CDW and/or superconductivity at zero field: $x = 0.05$ ($T_{cdw} = 90$ K, $T_c = 1.6$ K), and $x = 0.07$ ($T_c = 3.5$ K). At high magnetic fields, superconductivity is suppressed and we find that the spin–lattice relaxation rate is described by a modified Korringa relation with a doping-dependent Korringa factor. The large values of the extracted interaction parameters signify the importance of electron–electron interactions and/or the Se p- and Ti d-band contribution for these materials. This is a key ingredient to the superconductivity for these compounds.

2. Experimental details

Single crystals of Cu$_x$TiSe$_2$ were grown by the chemical iodine-vapor transport method and characterized by x-ray, transport, and susceptibility measurements [11]. The plate-like samples with average thickness of 30 $\mu$m along the $c$-axis were cut in rectangular shapes with approximate dimensions 4 mm x 2 mm. Parallel stacks of rectangular samples were placed in a rectangular-shaped copper coil for a better filling factor with the magnetic field $B$ applied along the $ab$ plane (parallel with the plates) for NMR measurements. Two doping levels ($x = 0.05, 0.07$) of Cu$_x$TiSe$_2$ were studied under the same conditions. $^{77}$Se and $^{63}$Cu NMR spectra, Knight shift, and spin–lattice relaxation rates were obtained using a home-built NMR spectrometer equipped with a high homogeneity 15 T sweepable magnet. $T_1$ was measured by the recovery of the spin echo intensity as a function of time after saturation.

3. Results and discussion

Figure 1(a) shows the representative $^{63}$Cu (spin-3/2, $\gamma_n = 11.285$ MHz T$^{-1}$, 69.1% natural abundance) NMR spectrum. The $^{63}$Cu NMR spectrum consists of two peaks, which are assigned to the signals from the sample and copper coil, as indicated in the figure. The symmetric, sharp spectral shape of the NMR signal indicates that the Cu site is not affected by CDW modulation. The insensitivity of $^{63}$Cu nuclei to an electronic state should be ascribed to the fact that the Cu atoms are located in between the TiSe$_2$ layers which are bounded by van der Waals interaction. Quadrupolar effects are expected for Cu nuclei which occupy a site of non-cubic symmetry but the satellites are not observable. The quadrupole frequency $v_Q$ for $^{63}$Cu is usually on the order of 20–30 MHz [14], thus the quadrupolar satellites are probably too broad and washed out due to disorder since Cu is dilute in this system. As such, the recovery of the longitudinal nuclear magnetization is appropriately fitted by the master equation for a spin-3/2 central transition using a single saturating pulse: $M_s(t) = M_0[1 - 0.1e^{-t/\tau} - 0.9e^{-t/\tau}]$ [15] (see figure 1(c) inset). The temperature dependence of the $^{63}$Cu NMR Knight shift and spin–lattice relaxation rate $1/T_1$ at 8 T is summarized in figures 1(b) and (c). The $^{63}$Cu Knight shift data exhibit very weak temperature dependence with $K_s \approx 0.080$% for $x = 0.05$ and $K_s \approx 0.088$% for $x = 0.07$, whereas in comparison $^{63}$Cu metal has $K_s = 0.2394$% [14]. There is no hint that its temperature dependence scales to the magnetic susceptibility. In addition, no anomalies are accompanied by the CDW transition. This might be due to the fact that the
corresponding 77Se NMR shift as a function of temperature. A single-alloy compound developed by Moriya [18] and later refined due to the effect of electron–electron interaction in metals and behaviors we invoke a model involving a Korringa factor $K = \frac{\gamma n}{\gamma_e} K_s (1)$ for the Cu TiSe$_2$ from [16]. Inset: log–log plot of 77$^1$/T$_1$ versus T.

external field of 8 T fully suppresses the residual CDW state by shifting the chemical potential and/or changing the electronic density of states of Ti 3d bands. The $^{63}$Cu spin–lattice relaxation rate for $x = 0.07$ varies linearly with temperature, obeying Korringa behavior with a slope approximately 1/18 times that of a pure $^{63}$Cu metal.

Since the Se atoms are located on the layers, they probe the Fermi surface and provide more information on electronic correlations in this material. Figure 2 displays the temperature dependence of 77Se (spin-1/2, $\gamma_n = 8.13$ MHz T$^{-1}$, 7.5% natural abundance) spectra and the NMR shift of the $x = 0.07$ compound at $B = 11.1$ T. The 77Se NMR signal shows the symmetric, sharp spectral shape as well. The NMR shift is constant from 280 to 150 K but increases monotonically upon further cooling. We note that the room temperature NMR shifts $K$ for the Cu$_x$TiSe$_2$ samples ($K \approx 0.141$% for $x = 5$% and $K \approx 0.15$% for $x = 7$%) are close to the reported NMR shift values of the selenide compounds TiSe$_2$ ($K_{iso} = 0.111$%) [16] and TaSe$_2$ ($K_{iso} = 0.162$%) [17].

In figure 3 we compare the temperature dependence of 1/$T_1$ of Cu$_x$TiSe$_2$ ($x = 0.05, 0.07$) single crystals with that of a 77Se metal [14] and powdered TiSe$_2$ [16]. A single-exponential fitting equation $M_r(t) = M_0[1 - e^{-\tau}]$ was used to extract the $T_1$ values from the magnetization recovery curves. It is apparent that an increase of the Cu doping concentration leads to an enhancement of the relaxation rate as well as an increase of the slope of the Korringa-like behavior. The inset of figure 3 shows the non-linear 1/$T_1$ versus $T$ behavior of the parent compound TiSe$_2$ and the subsequent linear behavior upon Cu doping which suppresses the CDW state. In order to understand the underlying mechanism of the observed 1/$T_1$ behaviors we invoke a model involving a Korringa factor $K(\alpha)$ due to the effect of electron–electron interaction in metals and alloy compounds developed by Moriya [18] and later refined by Narath and Weaver [19].

In simple metals, the dominant relaxation mechanism of nuclear spins is due to their interaction with conduction electron spins. This is given by the Korringa relation 1/$T_1 \propto T$ wherein only the Fermi contact interaction is taken into account for noninteracting electrons. However, electron–electron interactions cannot be neglected especially for metal alloys. The Coulomb interaction has an effect on the magnetic susceptibility which is proportional to the Knight shift $K_1$ [18, 19]. The internal magnetic field experienced by a nucleus is given by $H_{loc} = (H_{loc}) + \delta H$ where $(H_{loc})$ is the average internal magnetic field and $\delta H$ is the fluctuating magnetic field. The nuclear spin–lattice relaxation rate is a measure of the perpendicular fluctuating magnetic field $\delta H_{\perp}$ given by $1/T_1 = (\gamma_e)^2 \int_0^\infty dt \exp(i\omega t)\langle \delta H_{\perp}(t)\delta H_{\perp}(0) \rangle$. In metals with a strictly noninteracting electron gas, the relaxation rate is proportional to the temperature and square of the Knight shift [18], known as the Korringa relation:

$$1/T_1 = \left(4\pi n_k T \right) \frac{\gamma_n^2}{\gamma_e^2} K^2 (\alpha)$$

where $\gamma_n$, $\gamma_e$ are the nuclear and electron gyromagnetic ratios, respectively. Moriya modified the Korringa relation by incorporating the factor $K(\alpha)$ that includes the effect of a $\delta$-function-potential electron–electron interaction [18]:

$$1/T_1 = \left(4\pi n_k T \right) \frac{\gamma_n^2}{\gamma_e^2} K(\alpha)$$

where the Korringa factor $K(\alpha) = 2 \int_0^1 \frac{(1-\alpha)^2}{\ln(1-\alpha)} dx$ is a function of the interaction parameter $\alpha$, a measure of electron–electron interaction. Here $\alpha = \frac{2\pi n k}{\epsilon_F}$ and $G(x) = \left(\frac{1}{x} \right) [1 + \frac{1}{\sqrt{\pi}} \log \frac{1}{1 + x}]$ from the free electron approximation with $x = \frac{\epsilon}{\epsilon_F}$ where $\epsilon$ is a constant, $n$ is the number of electrons, $q$ is the wavevector, and $\epsilon_F, k_F$ are the Fermi energy and wavenumber, respectively [18]. The value of $K(\alpha)$ ranges from 0 to 1. For $\alpha = 0$, $K(\alpha) = 1$.

Figure 2. (a) Temperature dependence of 77Se NMR spectra of Cu$_x$TiSe$_2$ ($x = 0.07$) at 11.1 T for $B \parallel ab$-plane. (b) The corresponding 77Se NMR shift as a function of temperature.

Figure 3. Comparison of the temperature dependence of 77Se spin–lattice relaxation rates 1/$T_1$ for 77Se metal [14], Cu$_x$TiSe$_2$ ($x = 0.05, 0.07$) single crystals from this work, and the powdered parent compound TiSe$_2$ from [16]. Inset: log–log plot of 77$^1$/T$_1$ versus T.
By comparing our data with the enhanced Korringa factor electron–electron interactions based on 77Se NMR data in Cuδ contribution, and (at room temperature (see table 1) yield

In comparison, data from the parent compound TiSe2 [16] indicates that the exchange enhancement in the Cu metal is more dominant than in the Cu0.077Se data, which gives us equation (1). A corrected version was later formulated by Narath appropriate for alkali and noble metals where the function potential has a non-zero interaction range less than the atomic radius [19].

Before delving into the Korringa factor calculation, we note that the orbital shift contribution cannot, in the present case, be accurately separated from the spin part. Typically, the orbital contribution can be unambiguously determined in the superconducting state where the spin part of the shift vanishes at low temperature due to pairing. However, access of NMR in the superconducting state, believed to be of Bardeen–Cooper–Schrieffer (BCS) type [9], is hampered by the low upper critical field (Hc2 ~ 1 T) [3] of these compounds. We can, however, make some estimates based on the NMR data from the parent compound TiSe2 [16]. The total NMR shift K can be expressed as

\[ K = K_{sc} + K_{cp} + K_{vv} - \delta_{chem} \]  

where \( K_{sc} \) is the s-electron contact term, \( K_{cp} \) is the p-electron core polarization term, \( K_{vv} \) is the Van Vleck orbital contribution, and \( \delta_{chem} \) is the chemical shift. Experimental estimates from a previous 77Se NMR study on TiSe2 [16] at room temperature yield \( K_T \approx 0.111\% \), \( K_{sc} \approx 0.03\% \), \( |K_{cp}| \approx 0.01\% \) thus the temperature-independent part \( K_{vv} - \delta_{chem} \) is 0.071\%. Since Cu doping into the TiSe2 layers increases the density of states (DOS) at the Fermi level, this will increase \( K_{sc} \) and \( K_{cp} \), but the terms \( K_{vv} \) and \( \delta_{chem} \) should be unaffected since they do not depend on DOS. We can then estimate the spin part of the total shift for the Cu0.07TiSe2 system to be approximately \( K - 0.071\% \). This gives us the high temperature Knight shift values of 0.07\% for \( x = 5\% \) \( (K = 0.141\%) \) and 0.079\% for \( x = 7\% \) \( (K = 0.15\%) \) doping level (see table 1).

First we revisit the 63Cu data in figure 1 which yield \( K(\alpha) = 0.21 \), \( \alpha = 0.71 \) for \( x = 7\% \) and \( K(\alpha) = 0.51 \), \( \alpha = 0.42 \) for a pure 63Cu metal. The fact that \( K(\alpha, 63Cu) > K(\alpha, x = 7\%) \) indicates that the exchange enhancement in the Cu metal is more dominant than in the Cu0.07TiSe2 compound. For the 77Se data, \( K(\alpha) \approx 0.38 \), \( \alpha = 0.54 \) for \( x = 5\% \) and \( K(\alpha) \approx 0.42 \), \( \alpha = 0.51 \) for \( x = 7\% \) doping. The large value of \( \alpha \) highlights the significance of electron–electron interactions. In comparison, data from the parent compound TiSe2 [16] at room temperature (see table 1) yield \( K(\alpha) \approx 0.040 \), \( \alpha = 0.96 \). The small value of \( K(\alpha) \) for TiSe2 may suggest strong ferromagnetic correlations [20] but this compound is viewed as a correlated semiconductor which may warrant its deviation from this theoretical interpretation [21]. For the Cu0.07TiSe2 system, the result \( K(\alpha, x = 7\%) > K(\alpha, x = 5\%) > K(\alpha, x = 0\%) \) indicates that Cu intercalation monotonically increases the exchange enhancement in the Se site. In addition to correlation effects, the contribution of the DOS should also be considered in the observed relaxation behavior. Here Cu0.07TiSe2 compounds evolve into better metals as evidenced by decreasing resistivity and increasing susceptibility as Cu doping is increased [3, 11]. This points to the fact that increasing Cu content introduces carriers into the TiSe2 conduction band, increasing the DOS at the Fermi level [3] thereby enhancing the relaxation rates in agreement with our experimental data.

Table 1. Korringa factor \( K(\alpha) \) and interaction parameter \( \alpha \) due to electron–electron interactions based on 77Se NMR data in Cu0.07TiSe2 \((x = 0.05, 0.07)\) and TiSe2 [16] at room temperature.

| Cu0.07TiSe2 | \( \frac{1}{T}T \) (s K)\(^{-1} \) | \( K_{sc} \) (%) | \( K(\alpha) \) (Moriya) | \( \alpha \) (Narah) |
|-------------|----------------|---------------|----------------|----------------|
| x = 0% [16] | 0.0005 | 0.03 | 0.0401 | 0.955 | 0.99 |
| x = 5% | 0.0259 | 0.07 | 0.382 | 0.535 | 0.812 |
| x = 7% | 0.0363 | 0.079 | 0.42 | 0.505 | 0.782 |

4. Conclusion

We have presented 77Se and 63Cu NMR studies of Cu0.07TiSe2 \((x = 5\%, 7\%)\). We find that the 63Cu Knight shift shows weak variations with temperature and the spin–lattice relaxation rate 77Se 1/T\(_1\) follows a modified Korringa relation. The observed Korringa factor was discussed in terms of Moriya’s exchange-enhanced relaxation model and DOS contribution. Our results suggest that enhanced electronic correlations and Se p- and Ti d-hands play a key role in inducing superconductivity in the Cu0.07TiSe2 compounds.

Acknowledgments

This work is supported by the US National Science Foundation (NSF) DMR grant 0602859, Priority Research Center Program (2009-0093817) and Basic Science Research Program (2009-0077376) of Korea NRF, and the National Basic Research Program for China 2006CB922005. The experiments were...
performed at the National High Magnetic Field Laboratory which is supported by NSF DMR-0084183, by the State of Florida, and by the Department of Energy.

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