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Effect of pressure on the neutron spin resonance in the unconventional superconductor $FeTe_{0.6}Se_{0.4}$

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We have carried out a pressure study of the unconventional superconductor $FeTe_{0.6}Se_{0.4}$ up to 1.5 GPa by neutron scattering, resistivity, and magnetic susceptibility measurements. The neutron spin resonance energy and the superconducting transition temperature have been extracted as a function of applied pressure in samples obtained from the same crystal. Both increase with pressure up to a maximum at ≈1.3 GPa, directly demonstrating a correlation between these two fundamental parameters of unconventional superconductivity. A comparison between the quantitative evolution of T_c and the resonance energy as a function of applied pressure is also discussed. These measurements serve to demonstrate the feasibility of using pressure dependent inelastic neutron scattering to explore the relationship between the resonance energy and T_c in unconventional superconductors.

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Unconventional superconductors such as cuprates, heavy-fermion compounds, iron pnictides, and chalcogenides all share some notable features. Perhaps the most salient is the presence of static or dynamic magnetism throughout the superconducting region of the phase diagram.[1,2] A hallmark of this is a collective spin excitation that appears as a peak in the imaginary part of the dynamic susceptibility $\chi''(\mathbf{Q},\omega)$,[3–12] often called the spin resonance. This resonance is localized in both wave vector and energy transfer, and appears below the superconducting transition temperature. Although still open to interpretation,[13] a commonly held view is that this signal originates from a sign change of the superconducting order parameter on different parts of the Fermi surface.[14] This implies an unconventional mechanism with a repulsive interaction in momentum space, as opposed to the attractive interaction in BCS theory. Within this picture, the existence of the resonance is definitive evidence of unconventional superconductivity.[15] The observation of this signal in iron superconductors[9–12,16] provided further stimulus to explore the relationship between the resonance energy ω_r and other characteristic energy scales such as the superconducting transition temperature T_c or the superconducting gap Δ.[1,17–19]

Recent studies show that there is ambiguity in interpreting the relationship between T_c and ω_r,[18,19] in large part due to the difficulty in separating the intrinsic and extrinsic effects of chemical doping, such as disorder, inhomogeneity, and the influence of static magnetic order. Consequently, a clean tuning parameter such as pressure has the potential to avoid these complications and yield further insight into the relationship of the resonance and unconventional superconductivity. Unfortunately, pressure dependent inelastic neutron scattering measurements are notoriously difficult and to date we are unaware of any reported studies of the spin resonance as a function of applied pressure. Thus the work presented here provides a demonstration of an experimental approach to explore the relationship between the spin excitation spectrum and unconventional superconductivity.

The $FeTe_{1-x}Se_x$ family is a good candidate for such studies, as large single crystals can be grown and T_c shows a substantial sensitivity to applied pressure.[20,21] In particular, for compositions close to $x \approx 0.43$, the samples do not exhibit long-range magnetic order and T_c increases with pressure, reaching a maximum at ≈2 GPa,[22] a pressure amenable to a number of experimental techniques. Here, we present inelastic and elastic neutron scattering, resistivity, and magnetic susceptibility measurements of $FeTe_{0.6}Se_{0.4}$ ($T_c \approx 12$ K) up to 1.5 GPa. T_c and ω_r show a qualitatively similar behavior, although ω_r does not increase as much as T_c with increasing pressure, suggesting the lack of proportionality between these two energies.

The $FeTe_{0.6}Se_{0.4}$ crystal studied here was grown using a modified Bridgman technique.[23] The stoichiometry was determined by energy dispersive x-ray analysis, resulting in 1.02 ± 0.02 for Fe, 0.6 ± 0.02 for Te, and 0.4 ± 0.02 for Se. All the high pressure measurements were performed on samples from the same crystal growth (the same large single crystal). The inelastic neutron scattering experiments under pressure were performed on the HB-3 triple axis spectrometer at the High Flux Isotope Reactor of Oak Ridge National Laboratory (ORNL) with collimations of 48′-60′-80′-120′. A McWhan piston-cylinder pressure cell[24] was used with 3M FC-75 fluorinert as the pressure medium. A 0.5 g crystal was encapsulated in the inner BeCu neutron pressure cell ($\o \times h = 5$ mm × 10 mm) with the $[1\bar{1}0]$ direction vertical. Room temperature neutron powder diffraction was performed using the SNAP diffractometer at the Spallation Neutron Source at ORNL. NaCl powder was ground into a 0.8 g $FeTe_{0.6}Se_{0.4}$ sample to use as a pressure calibration standard. The sample was loaded into a Paris-Edinburgh press fitted with single toroid cubic boron nitride anvils, with the incident beam through the TiZr null scattering alloy gasket. Pressure was determined by application of the isothermal NaCl equation of state determined by Decker[25] to the refined lattice parameters obtained at each measured pressure from LeBail fits using the GSAS software suite.[26] High pressure resistivity measurements on a single crystal were performed in an easyLab Mcell 30. The electrical contacts were made using DuPont 4929N silver paste. The pressure was determined during the pressurization

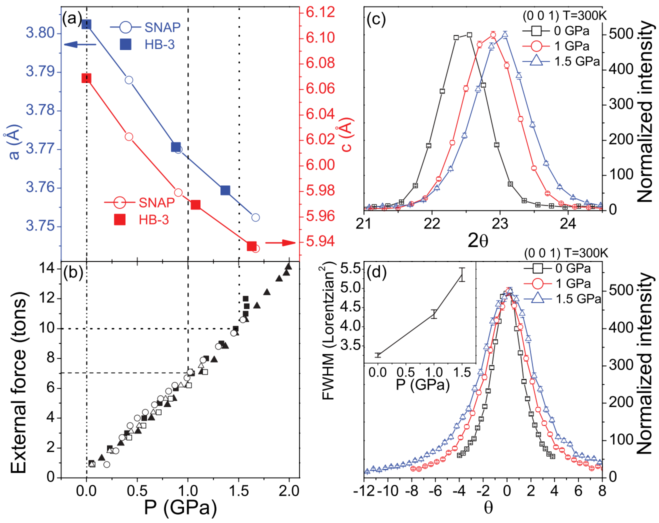

FIG. 1. (Color online) (a) Pressure dependence of the $FeTe_{0.6}Se_{0.4}$ lattice parameters a (in blue) and c (in red) measured by neutron powder diffraction on the time-of-flight diffractometer SNAP (open circles), and single crystal neutron diffraction on the triple axis spectrometer HB-3 (squares) for the single crystal used in the inelastic measurements. (b) Pressure calibration of the McWhan pressure cell as a function of the applied external force. (c) Pressure dependence of the θ-2θ scan on (001). (d) Evolution of the single crystal mosaic as a function of pressure. Inset: Lorentzian squared full width at half maximum (FWHM) as a function of pressure.

at room temperature with calibrated manganin wire and was also calculated from the applied load. Fluorinert (FC-75) was used as the pressure medium. The dc magnetization was measured on a single crystal by a commercial superconducting quantum interference device (SQUID) magnetometer (MPMS) in a BeCu piston cylinder cell using Daphne7373 as the pressure medium. The pressure was calibrated using the superconducting transition of Sn.

According to the different calibration tests for the McWhan pressure cell[24] (by measuring the resistance of a manganin wire under pressure), the chosen external forces applied on the pressure cell should result in room temperature pressures of ≈0, 1, and 1.5 GPa [Fig. 1(b)]. The lattice parameters of the large single crystal of $FeTe_{0.6}Se_{0.4}$ used for the inelastic measurements were extracted from θ-2θ scans through the (110) and (001) Bragg reflections [see Figs. 1(a) and 1(c)] at room temperature on the HB-3 spectrometer for the three different chosen pressure points (applied forces of, respectively, 1, 7, and 10 tons). The relative decrease of these lattice parameters are compared to the absolute values of these same lattice parameters obtained from neutron powder diffraction using the SNAP diffractometer. For this purpose, the first pressure point, ambient pressure/1 ton, was considered as a common reference and the HB-3 lattice parameters were normalized to the SNAP ones. The measured relative changes (from HB-3) were then compared to the lattice parameters extracted from the SNAP data [see Fig. 1(a)]. While the lattice parameter a shows higher values than expected from neutron powder diffraction for these pressures, the lattice parameter c shows slightly lower values, which suggests that the actual pressures at room temperature on the single crystal are close to the expected ones. One of the first visible effects of applied pressure, besides the reduction of the lattice parameters, is the broadening of the crystal mosaic. The rocking curves show a significant increase in their width [see Fig. 1(d) and the inset]. A Lorentzian-squared function provides a better description of the rocking curves than a classical Gaussian function.

In the $FeTe_{1-x}Se_x$ family, the neutron spin resonance has been shown to be two dimensional, centered at a **Q** of (1/2 1/2 L), where L indicates the irrelevant direction.[11] Above T_c, the spin excitations in $FeTe_{1-x}Se_x$ originate from an incommensurate wave vector near (1/2 1/2 L).[27] Below T_c there is a suppression of low energy spectral weight transferred to higher energy, resulting in the appearance of a resonance peak at $\omega_r \approx 6.5$ meV. Constant-Q scans at (1/2 1/2 L) were measured on the $FeTe_{0.6}Se_{0.4}$ crystal at 0, 1, and 1.5 GPa. The same superconductivity induced redistribution of spectral weight can be seen in the constant-Q scans under applied pressure, as seen in Fig. 2(b) for 1 GPa and Fig. 2(c) for

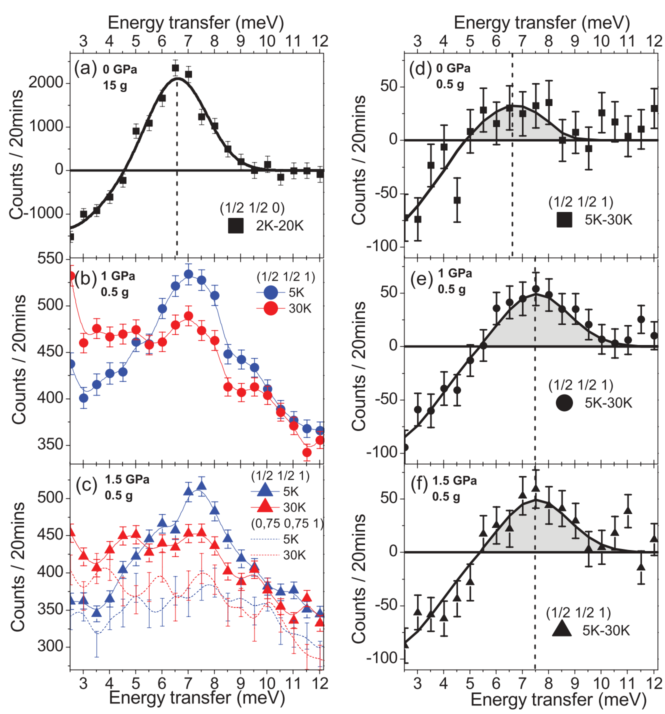

FIG. 2. (Color online) (a) Spin resonance in a 15 g single crystal of $FeTe_{0.6}Se_{0.4}$ with no applied pressure. Each point was measured for ≈7 min. The resonance energy is indicated by a vertical dotted line. (b)–(f) All data were measured on a 0.5 g single crystal of $FeTe_{0.6}Se_{0.4}$ in the pressure cell. (b) and (c) Constant-Q scans at (1/2 1/2 1) measured below T_c (5 K, blue) and above T_c (30 K, red) at, respectively, 1 GPa (circles, 80 min/point) and 1.5 GPa (triangles, 60 min/point). At 1.5 GPa, background constant-Q scans (dotted lines) measured at (0.75 0.75 1) for 20 min/point are shown for $T =$ 5 K (blue) and $T = 30$ K (red). (d) Spin resonance at 0 GPa. Each point was measured for 40 min. The resonance energy, the same as (a), is indicated by a vertical dotted line. (e) Same as (d) for 1 GPa and 80 min/point. (f) Same as (d) and (e) for 1.5 GPa and 60 min/point. The line and shaded area are the same as 1 GPa to emphasize the similar spectral weight and resonance energy for both pressures. Solid lines are a guide for the eye. All data were normalized to 20 min/point.

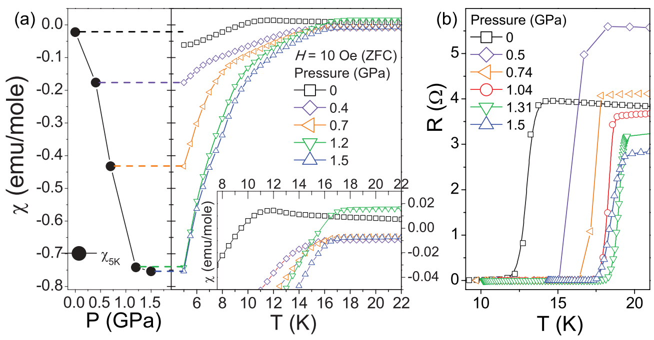

FIG. 3. (Color online) (a) Temperature dependence of magnetic susceptibility χ_{mag} for various applied pressure in the 0–1.5 GPa range. Inset: Zoom on $\chi_{\mathrm{mag}}(T)$ in the superconducting transition zone. Left panel: Lowest value of χ_{mag}, proportional to the screening effect in the sample. (b) Temperature dependence of electrical resistivity for various applied pressure in the 0–1.5 GPa range.

1.5 GPa. In each case there is a clear additional signal in the inelastic spectrum corresponding to the spin resonance. While the background introduced by the pressure cell is substantial, it is not insurmountable and is indicated in Fig. 2(c). This definitively shows the viability of such an experiment and that the resonance can be experimentally explored as a function of applied pressure.

The resonance signal is obtained by subtracting the data collected above T_c from the data collected below T_c. This procedure results in a positive difference centered at the resonance energy ω_r and an associated negative difference at lower energy corresponding to the opening of a gap in the spin excitation spectrum. Figure 2(a) displays this signal measured on a large single crystal of the same concentration outside of the pressure cell, indicating the expected resonance at $\omega_r = 6.6$ meV. For comparison, Fig. 2(d) shows the results of similar measurements on the 0.5 g sample (of the same concentration but different growth) within the pressure apparatus, confirming the presence of the resonance at the same energy. The effect of applied pressure on the resonance is illustrated by Figs. 2(e) and 2(f) (1 and 1.5 GPa, respectively). First, ω_r is shifted to a higher energy at 1 GPa ($\omega_r = 7.5$ meV), but does not increase further at higher pressure. Second, the spectral weight enhancement below T_c follows the same qualitative behavior as ω_r with a clear increase at 1 GPa and does not increase further at 1.5 GPa.

The large thermal mass of the pressure cell combined with long counting times prohibited an accurate determination of T_c from the onset of the resonance. Therefore the pressure dependence of T_c was determined from resistivity and magnetic susceptibility measurements on single crystal samples from the same growth as the crystal used for the inelastic neutron scattering measurements (see Fig. 3). Although different methods are commonly used to extract T_c from resistivity data, for completeness we adopt two metrics: (1) the onset of the drop in resistivity due to the appearance of superconductivity (T_c onset) and (2) the temperature at which the resistivity achieves the minimum value (T_c min).

The magnetic susceptibility data show broad transitions [see Fig. 3(a)], as previously observed for lower concentrations of Se ($x \leqslant 0.4$). In those cases, T_c is usually defined as the

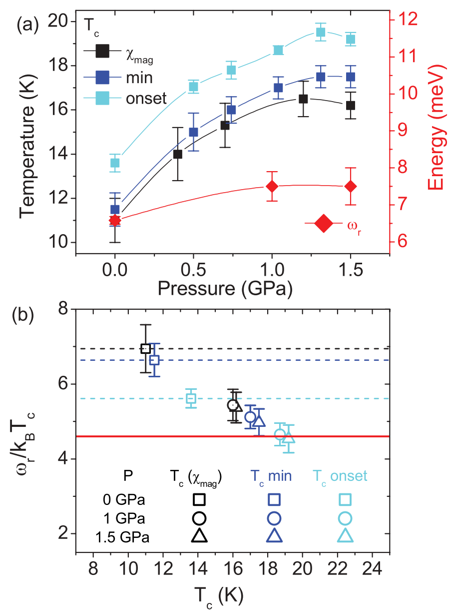

FIG. 4. (Color online) (a) Pressure dependence of ω_r (in red) and T_c as defined by the magnetic susceptibility (in black), and the resistivity (T_c min in dark blue, T_c onset in light blue). (b) T_c dependence of the ω_r/k_BT_c ratio of $FeTe_{0.6}Se_{0.4}$ for all pressures (squares for 0 GPa, circles for 1 GPa, and triangles for 1.5 GPa), and all definitions of the transition temperature. The horizontal dotted lines correspond to the value of ω_r/k_BT_c at 0 GPa for all three definitions of T_c. The horizontal red line corresponds to $\omega_r/k_BT_c = 4.6$, as previously observed for iron superconductors (Refs. 17 and 18).

temperature where χ_{mag} starts to decrease.[28] Although the broadness of the transition potentially indicates a distribution of T_c's, the energy of the resonance from the neutron scattering data is well defined, suggesting a unique bulk behavior.[29] For the following discussion, we will use the definition $T_c(\chi_{\mathrm{mag}})$ as described above. Although we believe our neutron scattering data is consistent with a narrow distribution of transition temperatures, we note that a hypothetical distribution of T_c's in our sample, together with a sharp resonance signal, can only be understood if the resonance energy and T_c are effectively decoupled.[29]

Here, as shown in Fig. 4(a), despite a constant offset in absolute value, T_c obtained from all three methods shows similar qualitative behavior, supporting the reliability of our definitions. At ambient pressure, previous measurements for this concentration suggest a T_c of about 14 K as extracted from the onset of resistivity. Our value of 13.6 ± 0.4 K is slightly less than this value. Such discrepancies are not uncommon, and this is precisely why we use pressure to overcome this problem by measuring the relative change of T_c in one sample rather than absolute values. Here, T_c increases with pressure by ≈50% at ≈1.3 GPa, and then remains constant or decreases slightly at higher pressures. Consistently, similar qualitative behavior was observed in other members of the $FeTe_{1-x}Se_x$ family.[20–22]

The lowest value of χ_{mag}, at the lowest temperature (5 K), is a manifestation of the screening effect in the sample. $\chi_{5\,\mathrm{K}}$ strongly decreases with applied pressure, reaching a plateau above ≈1 GPa [see Fig. 3(a), left]. This increased screening effect could indicate an enhancement of the superconducting volume fraction with pressure. As the strength of the resonance signal scales with superconducting volume fraction, we would expect a change in volume fraction would result in a change in inelastic neutron scattering intensity, as observed experimentally [see Figs. 2(d)–2(f)]. Whether the intensity increase is due to a changing volume fraction or is caused by a direct link between T_c and the resonance spectral weight remains unclear.

To provide further insight into the implications of our measurements we make the assumption that the T_c's which have been determined from bulk measurements are representative of the behavior of the large single crystal. Under this assumption $\omega_r(P)$ and $T_c(P)$ can be relevantly compared. Figure 4(a) displays such a comparison, where ω_r is expressed in units of kelvin and scaled by a constant to coincide with the lowest estimate of $T_c(P)$ at ambient pressure. Despite a qualitative similarity in the behavior of $\omega_r(P)$ and $T_c(P)$, the resonance energy does not increase nearly as rapidly as T_c. To further clarify this point, Fig. 4(b) shows the ratio ω_r/k_BT_c as a function of T_c. Both Figs. 4(a) and 4(b) suggest that ω_r is not proportional to T_c. This fact is independent of the definition we choose for T_c. These measurements show the feasibility of inelastic neutron scattering as a function of applied pressure for such studies, and future measurements will be of high interest to compare these results with other unconventional superconductors.

A comparison of this observation to the data obtained from multiple 122 materials[19] is particularly interesting. Contrary to the $FeTe_{1-x}Se_x$ family, these materials have a q_z dependent resonance mode where the ratio ω_r/k_BT_c is constant for $q_z = \pi$ and seems to vary with T_c for $q_z = 0$. Interestingly, the data presented in Fig. 4(b) is qualitatively similar to the $q_z = 0$ data for the 122 compounds. This suggests that when three dimensional, the resonance relevant for superconductivity, and which should be compared to either T_c or Δ, might be the one measured at $q_z = 0$.

It is worth noting that for the 122 materials, the highest ratios ω_r/k_BT_c (at $q_z = 0$) are obtained for the lowest concentrations of dopant, where electronic correlations are stronger. This is consistent with our observations of ω_r/k_BT_c decreasing with applied pressure in $FeTe_{0.6}Se_{0.4}$, as applying pressure likely increases orbital overlap and hybridization, implying a more itinerant and less correlated system. Within this context, the ratio of these energy scales relevant in unconventional superconductivity, ω_r/k_BT_c, seems to be an indication of the strength of the correlations in the system. This is also supported by higher observed ratios of ω_r/k_BT_c in cuprates, which are notoriously more correlated.[18]

Since the neutron spin resonance is often compared to the superconducting gap Δ,[1,18,19] it is interesting to examine the consequences of our results for the underlying pairing mechanism. Unfortunately, data of Δ as a function of pressure are lacking. Therefore we discuss our results in the context of a simple Hubbard model and consider the aforementioned model of sign change of the superconducting order parameter.[14] Within this context, a screened, on-site, intraorbital Coulomb interaction U renormalizes ω_r to a value lower than the energy of the particle-hole continuum 2Δ.[30,31] Pressure increases orbital overlap, effectively reducing U, and in turn increasing the ratio of $\omega_r/2\Delta$. In the very weak-coupling limit, we expect $\omega_r/2\Delta \approx 1$.[30,31] For either increasing or constant $\omega_r/2\Delta$, the observed decrease of ω_r/k_BT_c between 0 and 1 GPa implies a reduction of the superconducting pairing strength $2\Delta/k_BT_c$ (even though paradoxically the energy scale T_c has risen).

To conclude, this work further demonstrates that inelastic neutron scattering in conjunction with applied pressure is a powerful approach to unraveling the relationship between spin excitations and unconventional superconductivity. We have performed a pressure dependent study of the neutron spin resonance and superconducting transition temperature of an unconventional $FeTe_{0.6}Se_{0.4}$ superconductor up to 1.5 GPa. Free from any constraint induced by chemical substitution, we have shown that the energy and the intensity of the resonance increase with applied pressure up to 1 GPa and then stabilize. The similarity of this qualitative pressure dependent behavior with that of T_c confirms a correlation between those two characteristic energies and the important role of spin excitations in Fe-based unconventional superconductivity.

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