The crystalline electric field as a probe for long range antiferromagnetic order and superconductivity in CeFeAsO$_{1-x}$F$_x$

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We use inelastic neutron scattering to study the crystalline electric field (CEF) excitations of Ce$^{3+}$ in CeFeAsO$_{1-x}$F$_x$ (x = 0, 0.16). For nonsuperconducting CeFeAsO, the Ce CEF levels have three magnetic doublets in the paramagnetic state, but these doublets split into six singlets when Fe ions order antiferromagnetically. For superconducting CeFeAsO$_{0.84}$F$_{0.16}$ (T$_c = 41$ K), where the static AF order is suppressed, the Ce CEF levels have three magnetic doublets at $\hbar \omega = 0, 18.7, 58.4$ meV at all temperatures. Careful measurements of the intrinsic linewidth $\Gamma$ and the peak position of the 18.7 meV mode reveal clear anomaly at $T_c$, consistent with a strong enhancement of local magnetic susceptibility $\chi''(\hbar \omega)$ below $T_c$. These results suggest that CEF excitations in the rare-earth oxypnictides can be used as a probe of spin dynamics in the nearby FeAs planes.

The rare-earth (R) oxypnictides with general formula RFeAsO ($R =$ La, Sm, Ce, Nd, and Pr) are currently attracting much attention due to the discovery of high-transition temperature (high-$T_c$) superconductivity in these materials upon chemical doping \cite{1, 2, 3, 4, 5}. Al- though superconductivity is suppressed, the Ce CEF levels have three magnetic doublets at $\hbar \omega = 0, 18.7, 58.4$ meV at all temperatures. Careful measurements of the intrinsic linewidth $\Gamma$ and the peak position of the 18.7 meV mode reveal clear anomaly at $T_c$, consistent with a strong enhancement of local magnetic susceptibility $\chi''(\hbar \omega)$ below $T_c$. These results suggest that CEF excitations in the rare-earth oxypnictides can be used as a probe of spin dynamics in the nearby FeAs planes.

Our experiments were carried out using the MERLIN chopper spectrometer at ISIS facility, Rutherford-Appleton Laboratory, Didcot, UK \cite{16}; the BT4 Filter Analyzer Neutron Spectrometer (FANS) at the NIST center for neutron research (NCNR) \cite{17}; and the NG4 Disk-chopper time-of-flight spectrometer (DCS) at NCNR, Gaithersburg, Maryland. MERLIN is a high count rate, medium energy resolution, direct geometry chopper spectrometer with a large solid angle of position sensitive detectors. FANS is a high count instrument to measure inelastic excitations on powders and DCS is a cold neutron direct geometry chopper spectrometer. Our CeFeAsO and CeFeAsO$_{0.84}$F$_{0.16}$ samples were prepared using methods described in Ref. \cite{2} and their structural/magnetic properties are discussed in Ref. \cite{3}. For MERLIN measurements, a low temperature He-4 cryostat and closed cycle He-gas refrigerator were used for the temperature variable. The incident beam energies were $E_i = 7, 10, 30, 70, 105, 300$ meV. To separate the CEF magnetic scattering from phonon excitations, we also measured LaFeAsO and LaFeAsO$_{0.88}$F$_{0.08}$...
samples [4] as reference materials for phonon subtraction from the Ce samples. The data for CeFeAsO$_{1-x}$Fe$_x$ and LaFeAsO$_{1-x}$F$_x$ were converted to absolute units of mb/sr/meV/f.u. by normalizing the scattering from vanadium measurements made with the same incident energies. For the DCS measurements, we used a He-4 cryostat and an incident beam energy of 3.55 meV and for the FANS measurements we used a top-loading He-gas refrigerator.

Figure 1(a) shows the position of the Ce ion in the crystal structure environment of CeFeAsO. Relative to the Fe sublattice, the Ce$^{3+}$ ions are located alternately above and below the (AF ordered) Fe layers as shown in Fig. 1(b). Figures 1(c) and 1(d) summarize the Ce CEF excitation energies determined from our inelastic neutron scattering experiments for CeFeAsO and CeFeAsO$_{0.84}$F$_{0.16}$, respectively. According to neutron powder diffraction experiments [7], both CeFeAsO and CeFeAsO$_{0.84}$F$_{0.16}$ have a tetragonal (space group $P4/mnm$) crystal structure at room temperature. However, on cooling, CeFeAsO first exhibits a structural phase transition, changing the crystal symmetry from tetragonal to orthorhombic (space group $Cmma$), and then orders antiferromagnetically with a spin structure as shown in Figs. 1a and 1b [6,7]; CeFeAsO$_{0.84}$F$_{0.16}$ maintains the tetragonal structure for all temperatures and does not order magnetically above 4 K. In the tetragonal structure, the Ce atoms are located at the 2$c$ crystallographic site which has $C_{4v}$ point symmetry. This gives three non-zero CEF parameters in the crystal field Hamiltonian and its form in Stevens operators formalism is $H_{CEF}(C_{4v}) = B_{2g1}O_2^2 + B_{3g1}O_2^2 + B_{4g1}O_2^2$. In the case of the low-temperature orthorhombic structure of CeFeAsO, the Ce atoms are at the 4$g$ (0, 1/4, z) site which gives local point symmetry of $mnm$ ($C_{2v}$). The resulting Hamiltonian then involves five non-zero crystal field parameters as $H_{CEF}(C_{2v}) = B_{1g}O_2^2 + B_{2g}O_2^2 + B_{2g}O_2^2 + B_{4g}O_2^2 + B_{4g}O_2^2 + B_{4g}O_2^2$, where $B_{nm}$'s are the CEF parameters to be determined from the experimental data; and $O_{nm}$'s are operator equivalents obtained using the angular momentum operators [11].

We collected neutron scattering data on CeFeAsO and CeFeAsO$_{0.84}$F$_{0.16}$ on MERLIN and DCS spectrometers with different incident beam energies to search for Ce$^{3+}$ CEF excitations. To eliminate phonon scattering, we carried out identical scans using LaFeAsO and LaFeAsO$_{0.88}$F$_{0.08}$ as reference materials. Figures 2(a) and (b) show the phonon subtracted energy scans for CeFeAsO at 7 K and 200 K on MERLIN obtained with $E_i = 105$ meV. The inset of Fig. 2(a) plots similar data taken on DCS with $E_i = 3.55$ meV. Identical scans taken for CeFeAsO$_{0.84}$F$_{0.16}$ are shown in Figs. 2(c) and (d).
TABLE I: Refined \(B_n^m\) CEF parameters for CeFeAsO and CeFeAsO\(_{0.84}\)F\(_{0.16}\).

| CeFeAsO\(_{0.84}\)F\(_{0.16}\) CeFeAsO \((>T_N)\) CeFeAsO \((<T_N)\) |
|-----------------|-----------------|-----------------|
| \(B^0_2\)       | 2.29 ± 0.11     | 3.19 ± 0.15     | 1.648 ± 0.035 |
| \(B^1_2\)       | −0.061 ± 0.0064 | −0.032 ± 0.0072 | 0.1073         |
| \(B^2_4\)       | −3.098 ± 0.064  | −0.288 ± 0.009  |               |
| \(B^4_4\)       | 0.698 ± 0.023   | 0.755 ± 0.049   | 0.591 ± 0.018  |

We first discuss results on the superconducting sample as there are no complications of structural distortion and Fe magnetic order. To obtain the \(B_n^m\)'s CEF parameters in the \(H_{CEF}(C_{4v})\) Hamiltonian, we first used the FOCUS program, which has a Monte Carlo search routine, to fit the observed two CEF excitations at 18.7 meV and 58.4 meV in Figs. 2(c). We then fit many spectra simultaneously with different incident energies and temperatures using a CEF fit program and the results are plotted as solid lines in Figs. 2(c) and (d) for 7 K and 200 K, respectively. Tables I and II summarize the \(B_n^m\)'s CEF parameters and wave functions for CeFeAsO\(_{0.84}\)F\(_{0.16}\) obtained from those fits.

Comparing to the superconducting CeFeAsO\(_{0.84}\)F\(_{0.16}\), the Ce CEF excitations in CeFeAsO near 19 and 65 meV have clear double peaks at low temperature that become a single peak at 200 K [Figs. 2(a) and (b)]. In addition, the low-energy spectra in the inset of Fig. 2(a) shows a clear peak around 0.7 meV that is not present at 171 K. To understand this phenomenon, we carried out careful temperature dependence measurements of the \(\sim 19\) meV CEF excitation. Figure 3(a) shows the raw \(S(Q,\omega)\) spectra of CeFeAsO collected on MERLIN at 60 K using \(E_i = 30\) meV. After subtracting the phonon scattering background collected using LaFeAsO, the Ce CEF level shows two clear bands of excitations at 16.6 and 20.4 meV [Fig. 3(b)]. Figure 3(c) shows the detailed temperature dependence of the \(\sim 19\) meV excitations and Figure 3(d) plots splitting of the two low temperature peaks. Comparison of these figures with the Néel ordering temperature of CeFeAsO in Figure 3(e) makes it immediately clear that the CEF splitting is due to the long range AF Fe ordering [11].

In principle, the orthorhombic structural distortion that precedes the AF ordering in CeFeAsO can have an effect on the Ce CEF levels. However, since neutron powder diffraction data [7] showed that the Ce local environment is not much affected by the lattice distortion, we started fitting the low temperature spectra using the CEF parameters for tetragonal geometry, then added the effect of the molecular field of the Fe spins in the presence of the orthorhombic structural distortion. The solid line in Fig. 2(a) shows our fit to the data, and the CEF parameters for temperatures above and below \(T_N\) are also given in Table I. Assuming that the \([I, II, and III]$$ doublets in the paramagnetic state of CeFeAsO split into \([1\] to \([6\) singlets in the AF state as shown in Fig. 1(b), the observed excitations near 19 meV should be composed of 4 possible transitions \(|1\) → \(|3\), \(|1\) → \(|4\), \(|2\) → \(|3\), and \(|2\) → \(|4\). Since the transition probabilities \(|[1\) \(J_z \) (3)\]² and \(|[2\) \(J_z \) (4)\]² are rather small, the observed excitations at 16.8 and 20.4 meV in Fig. 2(a) actually arise from \(|1\) → \(|4\) and \(|2\) → \(|3\), and are controlled by the thermal population of \(|1\) and \(|2\), respectively. This is consistent with the temperature dependence of these two excitations, where the 16.8 mode decreases and the 20.4 meV excitation increases with decreasing temperature [Fig. 3(c)]. Therefore, the CEF energy levels for \(|3\) and \(|4\) should be at 16.6 + 0.7 = 17.5 meV and 20.4 meV, respectively.

In rare-earth substituted high-\(T_c\) copper oxides such as \(\text{Tm}_{0.1}\)Y\(_{0.9}\)Ba\(_2\)Cu\(_3\)O\(_{6+\delta}\) [13] and \(\text{Ho}_{0.1}\)Y\(_{0.9}\)Ba\(_2\)Cu\(_3\)O\(_7\) [14], the intrinsic linewidth \(\Gamma\) and peak position of the
TABLE II: Wave functions of different CEF levels for CeFeAsO$_{0.84}$F$_{0.16}$ and CeFeAsO above $T_N$.

|          | CeFeAsO$_{0.84}$F$_{0.16}$ | CeFeAsO ($> T_N$) |
|----------|---------------------------|-------------------|
| I        | $|\mp 1/2\rangle$         | $|\mp 1/2\rangle$ |
| II       | $-0.581|\mp 3/2\rangle + 0.814|\pm 3/2\rangle - 0.445|\mp 3/2\rangle + 0.895|\pm 3/2\rangle$ | |
| III      | $0.814|\mp 3/2\rangle + 0.581|\pm 3/2\rangle$ | $0.895|\mp 3/2\rangle + 0.446|\pm 3/2\rangle$ | |

The wave functions of different CEF levels are shown. The solid squares are MERLIN data while open squares are FANS data, both show clear anomaly at $T_c$. (c) The intrinsic linewidth $\Gamma(T)$ as a function of temperature. The solid line shows the expected $\Gamma_n(T)$ assuming noninteracting Fermi liquid. $\Gamma(T)$ deviates from $\Gamma_n(T)$ near $T_c$. (d) $\Gamma(T)/\Gamma_n(T)$ shows a clear anomaly near $T_c$, consistent with (c).

rare-earth CEF excitations are used to probe the local magnetic response of the CuO$_2$ planes and the formation of a superconducting energy gap. The CEF excitations of Ho and Er have also been used to study pseudogap and order-parameter symmetry in the underdoped superconducting HoBa$_2$Cu$_4$O$_8$ and ErBa$_2$Cu$_3$O$_{14.92}$, respectively [13]. To see if the $\hbar\omega_1 = 18.7$ meV CEF excitation in CeFeAsO$_{0.84}$F$_{0.16}$ is also sensitive to the occurrence of superconductivity, we carefully probed the temperature dependence of its intrinsic linewidth $\Gamma$ [Figs. 4(a), 4(c)] and peak positions [Fig. 4(b)]. Figure 4(a) shows the phonon subtracted data at different temperatures obtained on MERLIN with $E_i = 30$ meV. Figure 4(b) plots the peak position as a function of temperature, which shows a clear anomaly around $T_c$. Inspection of Fig. 4(c) reveals that the linewidth decreases with decreasing temperature. For the case when the CEF levels do not overlap, the temperature dependence of the linewidth $\Gamma(T)$ of the transition between the ground state ($|1\rangle$) and the first excited state ($|2\rangle$) in Fig. 1(c) can be accurately estimated using Eq.(1) in [14]. To first order, this can be written as $\Gamma(T) \propto \chi''(\hbar\omega_1) \coth(\hbar\omega_1/2k_BT)$, where $\chi''(\hbar\omega_1)$ is the local integrated magnetic susceptibility at $\hbar\omega_1 (=18.7$ meV) and $k_B$ is the Boltzmann constant [13]. To understand $\Gamma(T)$, we calculate the linewidth $\Gamma_n(T)$ below 150 K using this equation assuming a noninteracting Fermi liquid normal state [14], even though this is still under discussion. The solid line in Fig. 4(c) shows outcome of our calculation. The observed linewidth starts to deviate from the expected values near $T_c$, as shown more clearly in $\Gamma(T)/\Gamma_n(T)$ [Figure 4(d)]. The most natural interpretation of Figs. 3(c) and (d) is that the local integrated magnetic susceptibility $\chi''(\hbar\omega_1)$ from the Fe spin fluctuations at 18.7 meV increases dramatically below $T_c$. Since the temperature dependence of this excitation and its energy are rather similar to that of the neutron spin resonance recently observed in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ [18], we speculate that the observed linewidth change might be related to the spin resonance in CeFeAsO$_{0.84}$F$_{0.16}$.

In summary, we have determined the Ce CEF levels in nonsuperconducting CeFeAsO and superconducting CeFeAsO$_{0.84}$F$_{0.16}$ as a function of temperature. Our results show that Ce CEF excitations are very sensitive to the Fe magnetic order in the undoped system, and dynamic spin susceptibility in superconductor, and therefore can be used as a probe to study spin dynamical properties of the rare-earth based oxypnictides.

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