Fe K -edge X-ray resonant magnetic scattering from $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ superconductors

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Abstract. We present an X-ray resonant magnetic scattering study at the Fe- K absorption edge of the BaFe_2As_2 compound. The energy spectrum of the resonant scattering, together with our calculation using the full-potential linear-augmented plane wave method with a local density functional suggests that the observed resonant scattering arises from electric dipole ($E1$) transitions. We discuss the role of Fe K -edge X-ray resonant magnetic scattering in understanding the relationship between the structure and the antiferromagnetic transition in the doped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ superconductors.

1 Introduction

The 2008 discovery of superconductivity in $\text{LaFeAsO}_{1-x}\text{F}_x$ (up to $T_c = 26$ K with $x \approx 0.11$) [1] and $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ (up to $T_c = 38$ K with $x \approx 0.4$) [2] has generated tremendous excitement and led to extensive studies of the nature of superconductivity in these systems. The undoped parent compounds AFe_2As_2 ($A = \text{Ba}, \text{Sr}, \text{and Ca}$) of the superconductors form large, high-quality single crystals providing opportunities to researchers using neutron and X-ray scattering techniques. Over the past three years, neutron and X-ray measurements have revealed strong and unusual interconnections between structure, magnetism, and superconductivity.

The parent compounds AFe_2As_2 are poor metals and manifest a high-temperature tetragonal to a low-temperature orthorhombic transition that appears to be concomitant with a paramagnetic to antiferromagnetic (AFM) transition [3–7]. The structural transition temperature (T_S) and the AFM transition temperature (T_N) are suppressed to lower temperatures by hole doping with K on the Ba site, electron doping with transition metals (e.g., Co, Ni, Rh, Pt, and Pd) on the Fe site, or iso-electronic doping with P on the As site and Ru on the Fe site [2, 8–20]. Although both transitions remain coincident in superconducting samples produced by K doping, P doping, and Ru doping, [8–16] the structural and AFM transitions split with $T_S > T_N$ in electron-doped BaFe_2As_2 [2, 17–20]. When T_S and T_N are suppressed to sufficiently low temperatures, superconductivity emerges and coexists with AFM [17–19]. Furthermore, in Co-, Rh-, Ni- and Ru-doped BaFe_2As_2 , several neutron scattering measurements

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have witnessed an uncommon suppression of the magnetic order parameter in the superconducting state, which clearly indicates competition between AFM and superconductivity [13–16, 20, 21]. High-resolution X-ray diffraction measurements on Co-, Rh-, and Ru-doped BaFe_2As_2 have also revealed a suppression of the orthorhombic distortion below T_c consistent with a distinctive magnetoelastic coupling in the form of emergent nematic order proposed for the iron arsenides. For Co-doped BaFe_2As_2 , the re-entrance to the tetragonal structure has been observed [15, 20, 22].

For CaFe_2As_2 and SrFe_2As_2 , different experiment techniques [e.g. neutron scattering, X-ray scattering, muon spin resonance, and nuclear magnetic resonance (NMR)] have confirmed that the structural and magnetic transitions are coupled discontinuous (first-order) and hysteretic [4–6, 23]. However, in BaFe_2As_2 , some neutron measurements on polycrystalline samples showed a continuous (second-order) magnetic transition [7] while neutron scattering and NMR measurements on single crystals by others found a first-order magnetic transition and observed a large hysteresis upon cooling and warming [24, 25]. Wilson *et al.* initially reported that the structural and magnetic transitions in BaFe_2As_2 were second order in nature, [26] and the same group found later on annealed samples of BaFe_2As_2 that the orthorhombic distortion appeared as a second-order transition, interrupted, at slightly lower temperature, by a first-order transition to the low-temperature orthorhombic phase [27, 28].

This paper is organized as follows. In Sect. 2, we present our X-ray resonant magnetic scattering (XRMS) experimental details at the Fe K -edge of the undoped as-grown BaFe_2As_2 and our theoretical calculation of the XRMS spectrum. Finally, we discuss the application of Fe K -edge X-ray resonant magnetic scattering in understanding the relationship between the structure and the AFM transition in the doped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ superconductors and the nature of the transitions in the parent BaFe_2As_2 in Sect. 3.

2 General aspects of XRMS studies on $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$

2.1 Experimental details

The X-ray resonant magnetic scattering measurements were performed on the 6ID-B undulator beamline with top-up operation mode at the APS. The 6ID-B beamline uses a double-crystal Si (1, 1, 1) monochromator and the incident beam was 99.9% linearly polarized parallel to the storage ring plane with the resolution $(\Delta E/E) \sim 1 \times 10^{-4}$ (approximately 0.8 eV energy resolution at the Fe K -absorption edge). The spatial cross section of the incident beam was 1.0 mm (horizontal) $\times$ 0.2 mm (vertical). Temperature-dependent single-crystal X-ray diffraction measurements were performed using the same experimental configuration. The plate-like single crystals (see Refs. [9] for growth and characterization) with typical dimensions of $3 \times 3 \times 0.5 \text{ mm}^3$ were attached to a flat copper sample holder on the cold finger of a closed-cycle displacer refrigerator with the tetragonal (H , H , L) plane coincident with the vertical scattering plane [(0, 0, 1) - (1, 1, 0) scattering geometry]. Three beryllium domes were used to ensure a well-defined temperature of the sample down to 4 K, the base temperature of the refrigerator. The temperature was measured at a sensor mounted to the copper block holding the sample, and was stable within $\pm 0.002 \text{ K}$. Care was taken to minimize heating effects associated with the incident X-ray beam by measuring charge and magnetic reflections in close proximity and using the appropriate incident beam attenuation. The mosaicities of the BaFe_2As_2 and $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ single crystals were all less than 0.02° full width at half maximum (FWHM) as measured by the rocking curves of the (1, 1, 8) reflection at room temperature, attesting to the high quality of the sample.

Fig. 1. (a) Representative map of charge Bragg peaks related to four orthorhombic twin domains in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ with $x = 0.047$ below T_S . (b) $\mathbf{Q}$ scan through cut “A” marked in (a) for the undoped BaFe_2As_2 at $T = 6$ K. (c) Scattering measured in the $\sigma - \pi$ channel at the magnetic Bragg position.

For XRMS, we used the $\sigma - \pi$ polarization analysis. In the $\sigma - \pi$ channel, the incoming beam is linearly polarized perpendicular to the scattering plane and the component of the outgoing beam which is parallel to the scattering plane is measured. Polarization analysis in the $\sigma - \pi$ channel was performed using a Cu crystal. The $(2, 2, 0)$ reflection of the Cu analyzer crystal ($2d = 2.553 \text{ \AA}$) yields a diffraction angle of $2\theta = 86.1^\circ$ at the Fe K -edge. A suppression of charge and fluorescence background was achieved by approximately a factor of 200 relative to the magnetic scattering signal due to the analyzer crystal.

2.2 Orthorhombic twin domains and AFM Bragg peak

The BaFe_2As_2 compounds undergo a high-temperature tetragonal to a low-temperature orthorhombic structural transition. The orthorhombic structure is related to the tetragonal structure in the following way. The basal $\mathbf{a-b}$ plane of the orthorhombic structure is rotated by 45° with respect to the $\mathbf{a-b}$ plane of the tetragonal structure so the lattice parameter a_O ($a_O > b_O$) of the orthorhombic structure is approximately $\sqrt{2} \times a_T$ ($a_T = b_T$) of the tetragonal structure. The Miller indices $(H, K, L)_O$ in orthorhombic notation are given by $(h + k, h - k, l)_O$ with $(h, k, l)_T$ in tetragonal notation [e.g. $(2, 0, 8)_O = (1, 1, 8)_T$]. We will use orthorhombic indices throughout the paper. In the orthorhombic phase, twin domains are formed due to the orientational degeneracy of orthorhombic distortion (see Fig. 2 in Ref. [29]). This yields four Bragg peaks in close proximity as illustrated in Fig. 1(a) where the two left peaks with $H \sim 2.00$ are related to $(2, 0, 8)$ reflections and the larger lattice parameter a_O , whereas the two right peaks are related to $(0, 2, 8)$ reflections which arise from other domains and are related to the smaller lattice parameter ($b_O < a_O$) [7, 24, 26]. In cuts through the charge peak positions both types of Bragg peaks occur as shown in Fig. 1(b). However, in the corresponding cuts through magnetic peak positions only peaks on the left side related to the enlarged lattice parameter a_O are seen as demonstrated by the $(1, 0, 7)$ Bragg peak in Figs. 1(c) and 3(a). This is consistent with previous neutron measurements of the magnetic propagation vector $\mathbf{Q}_{\text{AFM}} = (1, 0, 1)$ in BaFe_2As_2 [4] and $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ with $x = 0.047$. The moment direction along the $\mathbf{a}_O$ direction is also similar in both compounds supported by the observation of

large dipole resonant magnetic scattering for the $(1, 0, 7)$ Bragg peak in the $\sigma - \pi$ XRMS channel [30]. Therefore, the observation of scattering at $(1, 0, 7)$ and the absence of scattering at $(0, 1, 7)$ is consistent not only with the propagation vector but also with the moment direction along the $\mathbf{a}_O$ in the magnetic structure of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$.

2.3 Measured XRMS spectra

To ensure that the observed Bragg peak at the $\mathbf{Q}$ position $(1, 0, 7)$ is magnetic in nature, we measured the energy spectrum associated with the resonant scattering from BaFe_2As_2 and the intensity at this $\mathbf{Q}$ position as a function of temperature. In Fig. 2(b) we show the raw data from energy scans at constant $\mathbf{Q} = (1, 0, 7)$ at $T = 6\text{ K}$, well below T_N . To determine the background at this scattering vector, energy scans were also performed at $(1, 0, 7)$ for $T = 140\text{ K}$, just above T_N , and at $\mathbf{Q} = (0.9, 0, 7)$, away from the magnetic peak, at $T = 6\text{ K}$. The shape of the background in the vicinity of the Fe K -edge is consistent with an increase in the fluorescence from the sample [Fig. 2(a)]. We subtracted the background from the energy scan measured at $T = 6\text{ K}$, corrected the energy scan for the absorption, and display it with close circles in Fig. 2(f). There are three distinctive features in the energy spectrum. First, an energy-independent contribution is most clearly visible below the absorption edge which arises from nonresonant magnetic scattering. Second, there is a noticeable dip in the scattering intensity just below the absorption edge, due to interference between the nonresonant and resonant magnetic scattering as the phase of the resonant scattering changes across the absorption edge. Third, we observed a sharp feature close to the absorption threshold and broad scattering that extends to energies more than 20 eV above the absorption edge. This broad energy spectrum is similar to what was observed in previous XRMS measurements in the $\sigma - \pi$ scattering channel at the Ni K -edge for NiO [31, 32] and can be attributed to the dipole channel from the $1s$ initial state to the unoccupied $4p$ states that are weakly polarized through hybridization with $3d$ states near the Fermi energy. The sharp feature close to the absorption threshold may also contain a contribution from quadrupole allowed channel from the $1s$ to $3d$ states, and our calculations (in the next section) suggest that the dipole contribution is the dominant one. However, an unambiguous separation of the dipole and quadrupole contributions will require further measurements of the angular dependence of the scattering as well as the $\sigma - \sigma$ scattering channel.

Figure 2(c) shows the magnetic order parameter as a function of temperature, measured at $(1, 0, 7)$. It shows that as the sample temperature increases, the intensity of the magnetic peak decreases until it can no longer be observed above background at approximately 140 K, in agreement with previous neutron-scattering measurements [7] and our neutron measurement. Together with the energy spectrum through the Fe K -absorption edge and the temperature dependent AFM order parameter, we conclude that the Bragg peak at $(1, 0, 7)$ is magnetic in nature.

2.4 Calculation of XRMS spectra

To model the resonant scattering spectra, we have used a full-potential linear-augmented plane-wave (FLAPW) method [33] with a local density functional [34]. To obtain a self-consistent charge and potential, we chose 810 $\mathbf{k}$ points in the irreducible Brillouin zone (IBZ), and set $R_{\text{MT}} \times k_{\text{max}} = 8.0$, where R_{MT} is the smallest muffin-tin radius and k_{max} is the basis set cutoff (the maximum value of $|\mathbf{k} + \mathbf{K}_i|$).

Fig. 2. (a) Measured fluorescence spectrum. (b) Energy scan through the (1, 0, 7) magnetic peak above (filled triangles) and below (filled circles) T_N , and at low temperature away from (1, 0, 7) (open squares). (c) Antiferromagnetic order parameter as a function of temperature measured by XRMS at the Bragg position (1, 0, 7) (filled circles) and measured with neutrons at the Bragg position (1, 0, 3) (open circles). (d) Calculated fluorescence spectrum. (e) Calculated XRMS due to dipole (black line) and quadrupole (red line) transitions. Note that the intensity from the quadrupole transition is about 5 orders of magnitude smaller than the dipole transition. (f) Theoretical XRMS spectrum (line) which is a sum of spectra from dipole and quadrupole transitions and corrected for interference. The experimental XRMS spectrum is corrected for absorption and the background is subtracted (close circles).

included in the basis). The muffin-tin radii are 2.4 a.u., 2.2 a.u., and 2.2 a.u. for Ba, Fe, and As, respectively. The self-consistent calculation was iterated until the total energy convergence reached 0.01 mRy/cell. For the X-ray absorption spectra [Fig. 2(d)] and XRMS [Figs. 2(e) and (f)] we calculated empty states up to 40 eV above the Fermi energy with 1320 $\mathbf{k}$ points in the IBZ and with the calculated self-consistent potential. To model the interference between the resonant and nonresonant

scattering close to the absorption edge, an energy-independent scattering amplitude which is equal to the resonant scattering contribution was added to the real part of the resonant scattering, based upon previous XRMS *K*-edge measurements which note a resonant enhancement of the magnetic scattering equal to the nonresonant magnetic scattering [31,32]. The calculated energy spectrum was broadened with a 1.25 eV Lorentzian [35] to account for the core-hole lifetime, and a 1 eV Gaussian for the instrumental resolution. The calculated absorption and resonant scattering spectra are displayed in Figs. 2(d)–(f). Our calculation of the quadrupole contribution to the sharp feature close to the absorption threshold indicates that it is much smaller than the dipole contribution [Fig. 2(e)]. The total XRMS in Fig. 2(f) captures the essential features of our measurements including the three features discussed in the previous section. Also a sharp peak from the quadrupole transition and broad features from the dipole transition in our calculation are consistent with what has been observed at the Ni *K*-edge for NiO [31,32].

3 Application of XRMS to nature of AFM order and transition

The observation of the AFM Bragg peak in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ compounds using the XRMS technique provides more understanding of the character of the structural and AFM transitions. For example, NMR measurements on underdoped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ with $x = 0.02, 0.04$ (Ref. [36]) and $x = 0.06$ (Ref. [37]) found a strong broadening of the ^{75}As lines attributable to the appearance of a distribution of internal fields in the magnetically ordered state. A quantitative comparison of the line broadening for $\mathbf{H} \parallel \mathbf{c}$ and $\mathbf{H} \perp \mathbf{c}$ led to the conclusion that there is a small incommensurability, ε , in the magnetic structure such that the incommensurate propagation vector in the lightly Co-doped compounds is given by $(1 - \varepsilon, 0, 1)$ with ε estimated to be approximately 0.04 reciprocal lattice units (r.l.u) which is the limit of the spatial Q resolution of thermal neutron measurements [37]. We applied XRMS to the $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ compounds and measured longitudinal and transverse scans through $(1, 0, 7)$ magnetic reflection. We observed a single peak at $T = 4.5 \text{ K} (< T_N = 47 \text{ K})$ in $\text{Ba}(\text{Fe}_{0.953}\text{Co}_{0.047})_2\text{As}_2$, whereas an incommensurability of magnitude ε would result in two peaks split by 2ε [Fig. 3(a)]. The FWHM of the single peak gives an upper limit for the potential incommensurability $\varepsilon \approx 4.9 \times 10^{-4}$ in the longitudinal direction and $\varepsilon \approx 4.7 \times 10^{-3}$ in the transverse direction. We also measured the longitudinal and transverse scans at $T = 20 \text{ K}$ (not shown) and did not find changes of FWHM [38].

Moreover, the current debate concerning the character of the structural and magnetic transitions in the parent BaFe_2As_2 compounds, as discussed above, has been resolved by our high-resolution X-ray diffraction and XRMS measurements. The results are summarized in Fig. 3(b). At $T = 137 \text{ K}$, we observed a sharp single peak which is consistent with a high-temperature paramagnetic tetragonal structure (Tet-PM) [bottom-left inset of Fig. 3(b)]. A second-order transition from the tetragonal to the orthorhombic phase occurs at $T_S = 134.5 \text{ K}$. At $T = 133.75 \text{ K}$, two additional peaks appear abruptly bracketing the two inner peaks [top-right inset of Fig. 3(b)]. The two inner peaks disappear gradually with cooling and the two outer peaks remain below 133.0 K [top-left inset of Fig. 3(b)]. The appearance of four peaks indicates that there coexist two orthorhombic phases: an orthorhombic phase associated with the two outer peaks and another phase associated with the two inner peaks.

We performed XRMS to investigate the relationship between the structural transition and AFM ordering in this system. As shown in the middle-right inset in Fig. 3(b), a single AFM peak appears at only one position of the four possible AFM positions denoted by red bars in the inset. It is noteworthy that these data at $T = 133.3 \text{ K}$

Fig. 3. (a) Longitudinal (left panel) and transverse (right panel) XRMS scans through a magnetic Bragg position (1, 0, 7) in $\text{Ba}(\text{Fe}_{0.953}\text{Co}_{0.047})_2\text{As}_2$ compounds. (b) Orthorhombic distortion as a function of temperatures for BaFe_2As_2 with insets showing different structural phases at different temperatures and the XRMS magnetic signal at the temperature where two orthorhombic phases coexist [see details of (b) in text].

required counting times of ~ 50 min per data point. Nevertheless, this observation allows us to conclude that the magnetic order is related only to the orthorhombic phase (Ort-AFM) associated with the two outer peaks. Taken together, a first-order magnetic transition at T_N drives the discontinuity in the structural order parameter at 133.75 K. Also, with further diffraction studies on Co-doped BaFe_2As_2 , we elucidated that the first-order AFM transition evolves to a second-order transition at approximately 2.2% Co concentration [28].

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