Magnetic ordering in EuRh$_2$As$_2$ studied by x-ray resonant magnetic scattering

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Element-specific x-ray resonant magnetic scattering (XRMS) investigations were performed to determine the magnetic structure of Eu in EuRh$_2$As$_2$ with the ThCr$_2$Si$_2$ structure. In the temperature range from 46 K down to the lowest achievable temperature of 6 K, an incommensurate antiferromagnetic (ICM) structure with a temperature dependent propagation vector $\tau \approx (0 0.09)$ coexists with a commensurate antiferromagnetic (CM) structure. Angular-dependent measurements of the magnetic intensity indicate that the magnetic moments lie in the tetragonal basal plane and are ferromagnetically aligned within the a-b plane for both magnetic structures. The ICM structure is most likely a spiral-like magnetic structure with a turn angle of $\sim 162^\circ (0.9\pi)$ between adjacent Eu planes in the c direction. In the CM structure, this angle is $180^\circ$. These results are consistent with band-structure calculations which indicate a strong sensitivity of the magnetic configuration on the Eu valence.

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The complex interplay between superconductivity, magnetism and structural instabilities in $A$Fe$_2$As$_2$ ($A =$ Ba, Sr, Ca, and Eu) pnictides upon chemical substitution, or under applied pressure has generated a great deal of recent attention and research activity in this ThCr$_2$Si$_2$-type tetragonal structure. In the temperature range from 46 K down to the lowest achievable temperature of 6 K, an incommensurate antiferromagnetic (ICM) structure with a temperature dependent propagation vector $\tau \approx (0 0.09)$ coexists with a commensurate antiferromagnetic (CM) structure. Angular-dependent measurements of the magnetic intensity indicate that the magnetic moments lie in the tetragonal basal plane and are ferromagnetically aligned within the a-b plane for both magnetic structures. The ICM structure is most likely a spiral-like magnetic structure with a turn angle of $\sim 162^\circ (0.9\pi)$ between adjacent Eu planes in the c direction. In the CM structure, this angle is $180^\circ$. These results are consistent with band-structure calculations which indicate a strong sensitivity of the magnetic configuration on the Eu valence.

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For the XRMS measurements, an as-grown plate-like single crystal with a surface perpendicular to the c axis and of approximate dimensions $1 \times 1 \times 0.1 \text{ mm}^3$ was selected. The sample shows very similar magnetic behavior to that previously reported. The XRMS experiment was performed on the 6ID-B beamline at the Advanced Photon Source at the Eu $L_\alpha$ absorption edge ($E = 7.611 \text{ keV}$). The incident radiation was linearly polarized perpendicular to the vertical scattering plane (\(\sigma\)-polarized) with a spatial cross-section of 1.0 mm horizontal ($\times 0.25 \text{ mm}$ vertical). In this configuration, resonant magnetic scattering rotates the plane of linear polarization into the scattering plane (\(\pi\)-polarization). In contrast, charge scattering does not change the polarization of the scattered photons (\(\sigma\)-\(\sigma\) scattering). Pyrolytic graphite PG (0 0 6) was used as a polarization and energy analyzer to suppress the charge and fluorescence background relative to the magnetic scattering signal. The sample was mounted at the end of the cold-finger of a dispex cryogenic refrigerator with the a-c plane coincident with the scattering plane and was measured at temperatures between 6 K and 50 K.

Figure 1 shows a scan along the (0 0 1) direction, measured at the peak of the dipole resonance (Fig. 2 at an x-ray energy $E = 7.614 \text{ keV}$ in the rotated $\sigma-\pi$ channel. At $T = 6 \text{ K} < T_N$, other than the allowed charge reflections (0 0 L) with L = even, new satellite peaks appear which can be indexed as (0 0 L) $\pm \pi$ with $\tau \approx (0 0.09)$, indicating an incommensurate magnetic structure (ICM). There are also weak peaks at (0 0 L) with L = odd pointing to an additional commensurate magnetic structure (CM) with propagation vector (0 0 1). Careful scans along (1 0 0) and (1 1 0) directions reveal no additional satellite peaks. To confirm the resonant magnetic behavior of these peaks, we performed energy scans through the Eu $L_\alpha$ absorption edge in the $\sigma-\pi$ channel (shown in Fig. 2 at 6 K. We observed one resonance peak...
approximately 3.5 eV above the absorption edge for both ICM and CM structures. This peak arises from dipole resonant scattering [17] and confirms that Eu is magnetic in EuRh$_2$As$_2$.

Figure 3(a) shows the temperature dependence of the integrated intensity of the ICM (0 0 6)+τ and (0 0 8)−τ satellite peaks, and the CM (0 0 3) Bragg reflection. The smooth variation of magnetic intensity close to the transition temperature indicates that the phase transition is second order. The integrated intensity ($I \sim \mu^2$, μ is the sublattice magnetization [18]) can be fitted with a power law of the form $I \sim (1 - \frac{T}{T_N})^{2\beta}$. The obtained exponents $\beta = 0.32 \pm 0.02$ and $\beta = 0.7 \pm 0.1$ for the ICM and CM peaks, respectively, will be interpreted later. The fitted transition temperature, $T_N = 46.0 \pm 0.5$ K, is in excellent agreement with the value $T_N = 46 \pm 1$ K, determined from the magnetization and heat capacity measurements.[9]

Figure 3(b) shows the temperature dependence of the propagation vector after correcting for the thermal expansion of the lattice. The propagation vector varies smoothly from 0.905c* at 6 K to 0.885c* at 46 K, supporting further the incommensurate nature of the ICM structure.

We now turn to the determination of the magnetic moment configuration. For the crystallographic space group $I4_{1}/mmm$ and propagation vectors of the form (0 0 γ), two independent magnetic representations are possible with moments that are either strictly along the c direction or confined to the a-b plane.[19] For a second order phase transition, Landau theory predicts that only one of the two above-mentioned representations is realized at the phase transition.[19] To differentiate between these two representations, a series of CM and ICM Bragg reflections were measured. Figure 4(a) shows the expected angular dependence of the magnetic intensity for the two above-mentioned representations along with the observed intensities. The XRMS intensity for the current experimental configuration can be calculated as:[20]

$$I = B \left( \frac{\mu_0 \cos \theta}{\sin 2\theta} \right)^2, \text{ for } \mu \text{ in the a-b plane}$$

$$= B \left( \frac{\mu_c \sin \theta}{\sin 2\theta} \right)^2, \text{ for } \mu \parallel c$$

(1)

where $B$ is a scaling factor, $\theta$ is the Bragg angle, $1/\sin 2\theta$ is the Lorentz factor and $\mu_0$ and $\mu_c$ are the components of magnetic moments along the a and c directions, respectively. Since the model calculation with the magnetic moment in the a-b plane closely agrees with the observed intensity, we conclude that the magnetic moments lie in the a-b plane for both the ICM and CM structures.

Both a transverse amplitude modulated collinear antiferromagnetic structure and a basal plane spiral antiferromagnetic structure are consistent with moments in the a-b plane and a propagation vector of (0 0 0.9). In an XRMS experiment one cannot distinguish between these two structures due to the presence of domains. However, we note that a spiral-like structure can persist down to the lowest temperature whereas a transverse amplitude modulated magnetic structure must transform to a square-wave modulation due to the expected equal amplitude of ordered magnetic moments at low temperatures. Such a “squaring up” of the magnetic structure would produce third harmonic satellite peaks ±3τ at $T = 6$ K, which were not observed (see Fig. 1). Therefore, we conclude that the ICM structure is a spiral-like structure with ferromagnetically coupled moments in each a-b plane and a temperature dependent turn angle of ∼162° (0.9π) between adjacent Eu planes. For the CM structure, the magnetic moments are also ferromagnetically aligned within the a-b plane. The observation of CM Bragg reflections at (0 0 L) with L odd, together with the absence of a ferromagnetic signal in magnetization measurements[9] indicate that the magnetic moments in the adjacent Eu planes are aligned in opposite directions for the CM structure.

We now turn to the discussion of certain subtle features observed in the XRMS study. First of all, from Fig. 1 we note that the Full-Width-at-Half-Maximum (FWHM) for pairs of satellite reflections, for example (0 0 4)±τ, is quite differ-
ent and there is an overall increase in FWHM with increasing scattering angle. Such features in FWHM can be explained assuming a variation in the lattice parameter $\Delta c \sim 0.05 \text{ Å}$, and a related variation in the propagation vector $\Delta \tau \sim 0.03c^*$. Simultaneous variations in both $c$ and $\tau$ compensate each other for the positions of the $+\tau$ satellite peaks and result in an unchanged FWHM. The effect is opposite for the $-\tau$ satellites, yields a strong variation in the positions for the $-\tau$ satellites and, therefore, increases the FWHM significantly. Indeed, the variation in the lattice parameter and corresponding inhomogeneity in the sample is also evident from the linear increase of FWHM of different charge peaks as a function of $L$ [see Fig. 3b)] as $\Delta L \approx \frac{\Delta c}{c} L$ and gives $\Delta c \sim 0.05 \text{ Å}$. Here we note that effects other than the variation in lattice parameter, such as strain in the sample, also affect the FWHM as a function of scattering angle.

Next, we turn to the observed coexistence of ICM and CM structures over the investigated temperature range. In rare earth intermetallic compounds such as EuPd$_2$Si$_2$ and EuCu$_2$Si$_2$, a minor phase has been observed which also orders magnetically at low temperatures with a slightly lower Eu valence than in the main phase.[$^{[24,25,26]}$]

To further investigate the effect of the Eu valence on magnetic ordering, we have performed band-structure calculations of the generalized susceptibility $\chi(q)$ for different valences of Eu by varying the Fermi energy. In the $\chi(q)$ calculation each small tetrahedron contribution (in $q$ space) was weighted by the Eu 5$d$ wavefunction components which are predominantly responsible for coupling the Eu 4$f$ moments via the RKKY mechanism. These calculations were performed using the full-potential linearized augmented plane-wave (LAPW) method with $R_{MT}K_{max} = 8$ and $R_{MT} = 2.5$, 2.2, and 2.2 a.u. for Eu, Rh, and As, respectively. We used 405 $k$-points in the irreducible Brillouin zone for the self-consistent charge and 34061 $k$-points in the whole reciprocal unit cell for the the $\chi(q)$ calculations. For the local density functional, the
Perdew-Wang 1992 functional\cite{27} was employed. The convergence criterion for the total energy was 0.01 mRy/cell.

In Fig. 5, a distinct peak is evident in $\chi(q)$ at $q = (0 0 1)$ for divalent Eu and the peak moves progressively to lower values of $q$ as the valence is increased (see inset to Fig. 5 for details). We note the presence of additional local maxima around $q = (0 0 0.6)$ and the zone center. Rather than attempt a detailed treatment of RKKY matrix elements, we have calculated the total energy of the virtual crystal with Eu$^{+2.1}$ for ferromagnetic ($q = 0$) and antiferromagnetic ($q = (0 0 1)$) ordering, and find that the CM phase to be 9.0 meV lower in energy; thus eliminating $\chi(q = 0)$ peak from consideration. Therefore, band structure calculations together with the observed coexistence of CM and ICM phases indicate a delicate energy balance between different magnetic configurations in EuRh$_2$As$_2$ and makes this compound a promising candidate for studying the complex interplay between changes in valence and magnetism as a function of external parameters.

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{(Color online) The generalized susceptibility $\chi(q)$ for different valence of Eu in EuRh$_2$As$_2$. The inset shows an expanded view of $\chi(q)$ close to the Brillouin zone boundary at $q = (0 0 1)$.}
\end{figure}

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