Magnetism of the Fe$^{2+}$ and Ce$^{3+}$ sublattices in Ce$_2$O$_2$FeSe$_2$: a combined neutron powder diffraction, inelastic neutron scattering and density functional study

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The discovery of superconductivity in the 122 iron selenide materials above 30 K necessitates an understanding of the underlying magnetic interactions. We present a combined experimental and theoretical investigation of magnetic and semiconducting Ce$_2$O$_2$FeSe$_2$ composed of chains of edge-linked iron selenide tetrahedra. The combined neutron diffraction and inelastic scattering study and density functional calculations confirm the ferromagnetic nature of nearest-neighbour Fe – Se – Fe interactions in the ZrCuSiAs-related iron oxyselenide Ce$_2$O$_2$FeSe$_2$. Inelastic measurements provide an estimate of the strength of nearest-neighbor Fe – Fe and Fe – Ce interactions. These are consistent with density functional theory calculations, which reveal that correlations in the Fe–Se sheets of Ce$_2$O$_2$FeSe$_2$ are weak. The Fe on-site repulsion $U_F$, is comparable to that reported for oxyarsenides and K$_{1-x}$Fe$_2-y$Se$_2$, which are parents to iron-based superconductors.

1. INTRODUCTION

The discovery of iron-based superconductivity$^{[1-4]}$ with transition temperatures as high as 55 K$^{[5]}$ has prompted efforts to understand both the electronic structure and magnetism of these materials, which are interrelated with superconductivity$^{[6-8]}$. The first class of iron-based superconductors reported, the 1111 family, derive from LnFeAsO (Ln = trivalent lanthanide). They adopt the ZrCuSiAs structure$^{[9]}$, composed of layers of edge-sharing O$_{Ln4}$ tetrahedra alternating with layers of edge-sharing FeAs$_4$ tetrahedra. A second class, 122 materials, derive from AFe$_2$As$_2$ (A = Ca, Ba) with the ThCr$_2$Si$_2$ structure$^{[10]}$, which again contains layers of edge-sharing FeAs$_4$ tetrahedra. The metallic parent phases in both classes undergo structural phase transitions from tetragonal to orthorhombic symmetry just above an antiferromagnetic (AFM) ordering temperature ($T_N = 137$ K for LaOFeAs$^{[11]}$ and $172$ K for CaFe$_2$As$_2$$^{[12]}$) with small ordered moments on the Fe sites in the $ab$ plane. Superconductivity has also been observed in the binary iron chalcogenide systems: the properties of Fe$_{1+x}$Te are very sensitive to the iron content$^{[13]}$ and superconductivity can be induced by S or Se doping$^{[14]}$; α-FeSe does not order magnetically and undergoes a transition to a superconducting state at 8 K at ambient pressure$^{[15]}$, or 37 K at 7 GPa$^{[16]}$. Recently, attention has turned to the potassium-iron-selenide phase diagram, in particular, K$_{0.8}$Fe$_{1.6}$Se$_2$, which adopts a vacancy-ordered ThCr$_2$Si$_2$ structure. This material is semiconducting$^{[17,23]}$ and orders antiferromagnetically below 559 K. Interestingly, the ordered Fe$^{2+}$ moments are large (3.31 $\mu_B$) and are oriented perpendicular to the layer, in contrast to the 1111 and 122 materials$^{[24]}$.

The magnetism of the iron sublattice in these materials has been the focus of much study in recent years. Initial studies on the 1111 and 122 materials suggested that the observed stripe magnetic ordering (ferromagnetic stripes along [010] in the orthorhombic unit cell)$^{[25,26]}$ arises from the competing nearest-neighbor (nn) and next-nearest-neighbor (nnn) AFM interactions$^{[27,28]}$. Subsequent work has highlighted the roles of other factors which lead to the complexity of the magnetic phase diagram for these materials$^{[6,29]}$.

In LnFeAsO and LnMnAsO materials, the Ln$^{3+}$ ions have a significant role not only in tuning the superconducting transition temperature in the doped phases (e.g. $T_c = 26$ K for LaFeAsO$_{1-x}$Fe$_x$$^{[1]}$, and 55 K for SmFeAsO$_{1-x}$Fe$_x$$^{[5]}$), but also in influencing the magnetism in the undoped parent phases. For example, the Fe$^{2+}$ moments of CeFeAsO order antiferromagnetically in the $ab$ plane at $T_N, Fe = 140$ K$^{[25]}$ while the Ce$^{3+}$ moments couple strongly with the Fe$^{2+}$ moments at relatively high temperatures$^{[30]}$, before developing a long range order below $\sim 3.7$ K with moments predominantly in the $ab$ plane$^{[25]}$. Recent studies suggested some re-orientation of the Fe moments within the $ab$ plane at the onset of the long range order of the Ce moments$^{[31]}$. The Ce$^{3+}$ ions influence the iron magnetic sublattice, and can also induce exotic properties such as Kondo screening of the local moment in closely-related CeFePO$^{[32]}$ and CeRuPO$^{[33]}$.

The synthesis and crystal/magnetic structures of the iron oxyselenide Ce$_2$O$_2$FeSe$_2$ were reported in 2011$^{[34]}$. It adopts a ZrCuSiAs-related structure in which the transition metal sites are half occupied by Fe$^{2+}$ cations in a stripe ordered structure (Fig.1). The magnetic structure of Ce$_2$O$_2$FeSe$_2$ (Fig.1b) determined from neutron powder diffraction (NPD) data reported rather surprising observations$^{[34]}$. It undergoes an AFM ordering below $T_N = 171$ K in which the Fe$^{2+}$ spins have a ferromagnetic (FM) order within each chain of edge-sharing FeSe$_4$...
tetrahedra despite the Fe-Se-Fe angle (71.94°) deviating strongly from 90° (Fig. 1b), so one would have expected an AFM ordering according to the Goodenough-Kanamori rule [35–37]. In the present work we re-examine the magnetic ordering in Ce$_2$O$_2$FeSe$_2$ to confirm these unusual observations on the basis of NPD and inelastic neutron scattering (INS) experiments as well as density functional theory (DFT) calculations. The paper is divided into five sections including this introduction; experimental and calculation descriptions; experimental and theoretical results; and finally a discussion and conclusion.

2. EXPERIMENTAL DETAILS

Ce$_2$O$_2$FeSe$_2$ was prepared as a black, polycrystalline sample (2.48 g) as described previously [34]. Preliminary characterisation was carried out using a Bruker D8 X-ray diffractometer (reflection mode, Cu Kα$_1$/Kα$_2$ radiation, Lynxeye Si strip position sensitive detector, step size 0.02° with variable slits) equipped with an Oxford Cryosystems Phenix cryostat. NPD data were collected on the high-flux D20 diffractometer at Institut Laue Langevin (Grenoble, France) with neutron wave-length 2.41 Å. The sample was placed in a 6 mm cylindrical vanadium can (to a height of ~4 cm) and cooled to 2 K. Data were collected over a 2θ range of 5–130° at 2 K intervals on warming to 200 K. Powder diffraction data were analyzed by the Rietveld method [38] using the TOPAS Academic software suite [39, 40] controlled by local routines. The diffractometer zero point and neutron wavelength were initially refined using data collected at 12 K with lattice parameters fixed at values determined previously [34]. The zero point and wavelength were then fixed in all subsequent refinements. Typically, the background was refined for each data set as well as the unit cell parameters and a Caglioti description of the peak shape. Structural characterization using data collected on the HRPD diffractometer at ISIS revealed no structural changes in this temperature range (4 – 218 K) [34], so the atomic coordinates were fixed and this work focuses on the magnetic ordering. The web-based ISODIS TORT software [41] was used to obtain a magnetic symmetry mode description of the magnetic structure; magnetic symmetry mode amplitudes were then refined to determine the magnetic structures.

The same polycrystalline sample was used for INS measurements. The sample was packed into an Al foil envelope and placed in an Al can. Two experiments were performed using the MARI direct geometry chopper instrument at ISIS. The sample was cooled to 5 K in a closed-cycle cryostat. The energy of the incident beam, $E_i$, was selected using a Gd Fermi chopper spinning at 150 Hz (for $E_i = 40$ meV) or 400 Hz (for $E_i = 150$ meV). In addition, a $\tau$ chopper was used to block fast neutrons and a thick disk chopper (spinning at 50 Hz) was used to improve background from neutrons above the Gd absorption edge. The cold triple-axis spectrometer SPINS at NIST Center for Neutron Research (Gaithersburg, USA) was used to investigate the temperature dependence of the crystal fields. A pyrolytic graphite (PG) monochromator (004 reflection) was used on the incident beam to give good resolution at high energy transfers and a PG(002) analyzer (horizontally focused over 11°) was tuned to select a fixed final energy of $E_f = 5.0$ meV. A Be filter was used on the scattered side.

In our DFT electronic structure calculations for Ce$_2$O$_2$FeSe$_2$, we employed the projected augmented-wave (PAW) method encoded in the Vienna ab initio simulation package [42–44], and the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof [45] for the exchange-correlation corrections, the plane wave cutoff energy of 500 eV, and the threshold of self-consistent-field (SCF) energy convergence of $10^{-8}$ eV. We extract four spin exchange parameters by employing five ordered spin states defined on a $(a, 2b, c)$ supercell (see below). The irreducible Brillouin zone was sampled with $4 \times 2 \times 1$ k-points. To describe the electron correlation associated with the 3d states of Fe and the 4f states of Ce, the DFT plus on-site repulsion U (DFT+U) [46] cal-

FIG. 1. [color online] (a) Orthorhombic nuclear unit cell and (b) monoclinic magnetic unit cell of Ce$_2$O$_2$FeSe$_2$ (Ce = green, Fe = blue, O = red, and Se = yellow spheres). (c) An isolated sheet of edge-sharing chains of FeSe$_4$ tetrahedra present in Ce$_2$O$_2$FeSe$_2$. (d) Zoomed-in view of the magnetic ordering in the Fe and Ce sublattices of Ce$_2$O$_2$FeSe$_2$. For convenience of discussion, the directions of the orthorhombic unit cell are used to describe the magnetic structure in (c) and (d); the FM chains of edge-sharing FeSe$_4$ tetrahedra lie in the ab-plane with the FM chains running along the a-direction.
3. RESULTS

In this section we outline the experimental and computational results of this paper. We first discuss the neutron diffraction results probing the magnetic structure followed by a section discussing inelastic neutron results from which exchange constants between the Fe ions and the Ce ions are derived. Finally, these are compared with density functional calculations.

A. Neutron powder diffraction

Rietveld analysis of NPD data collected at 250 K are consistent with the Fe-ordered, orthorhombic crystal structure described above. Additional reflections observed below $T_N$ are consistent with the magnetic ordering (and propagation vector $\mathbf{k} = (0 \frac{1}{2} \frac{1}{2})$) reported previously [24] and were indexed using an $a_n \times 2b_n \times 2c_n$ supercell (where the subscript $n$ refers to the nuclear unit cell); $hkl$ indices given subsequently for magnetic reflections refer to this magnetic unit cell. The intensity of these reflections increases smoothly on cooling to $\sim 100$ K. Below this temperature, some reflections (e.g., (0 1 1), (0 1 9), (0 3 3)) continue to increase in intensity, others (e.g., (0 1 5), (0 1 7), (2 1 1)) decrease slightly (Fig.2), while some additional very weak reflections (e.g. (1 1 1), (1 1 3)) are observed below this temperature.

The NPD data collected below $\sim 170$ K can be fitted by the nuclear structure and a magnetic phase composed of FM chains of edge-sharing FeSe$_2$ tetrahedra, with AFM coupling between adjacent FM chains (Fig.1b). Attempts to fit the data with models containing AFM chains were not successful. The “symmetry adapted ordering mode” approach [14] was used here to describe the magnetically ordered structure. Mode inclusion analysis (described elsewhere, [17]) was used to confirm that this arrangement of Fe moments gives the best fit to the data and does not change below $T_N$. Other models, including those with AFM chains, gave significantly worse fits. Whilst this FM-chain model gives magnetic Bragg peaks in the observed positions, the fit to the peak intensities was not perfect. Mode inclusion analyses were carried out at lower temperatures (80 K, 4 K) and confirmed that the arrangement of Fe$^{2+}$ moments does not change on cooling. Given the large ordered moment on the Fe sites in Ce$_2$O$_2$FeSe$_2$, we would expect our refinements to be sensitive to slight reorientations of the Fe$^{2+}$ moments, but there is no indication that reorientation of the Fe$^{2+}$ moments occurs. This is in contrast to the related PrFeAsO in which the Fe moments cant slightly along c at the onset of Pr$^{3+}$ ordering [18].

FIG. 2. [color online] Temperature-dependence of the magnetic Bragg reflections: (a) Sum of the intensity of the 17 strongest magnetic reflections. (b-e) The intensity of the (0 1 1), (0 1 3), (0 1 5) and (1 1 3) reflections (hkl indices refer to the $a_n \times 2b_n \times 2c_n$ magnetic unit cell) from the sequential refinements using a Pawley phase to fit the magnetic reflections. (f) Evolution of the Fe$^{3+}$ (blue, solid) and Ce$^{3+}$ (green, open) magnetic moments on cooling from Rietveld refinements. The solid black line shows fit to the function $M_T = M_0(1-(T/T_N)^\beta)$ for the Fe data between 100 - 171 K with $M_0, \mu_B = 3.40(4)$ $\mu_B$, $T_N = 175.5(8)$ K and $\beta = 0.28(1)$.

Whilst the FM-chain model gives a better fit than AFM-chain models, further analysis indicated that including the Ce magnetic ordering modes improves the fit significantly ($R_{wp}$ decreases from 5.49% to 4.37% at 80 K, and from 7.19% to 4.61% at 4 K for one additional parameter). Refinements are very sensitive to the relative signs of the Fe$^{2+}$ and Ce$^{3+}$ magnetic ordering mode amplitudes. For example, as measured by $R_{wp}$, a surface plot showing fit for different amplitudes of the Ce and Fe magnetic ordering modes indicates that the best fit is obtained when both modes have the same sign, corresponding to a FM coupling between nn Fe and Ce sites (see Supplementary Material). Refinement profiles and details are shown in Fig.3. If canting of the Ce moments is included in the model, the Ce moments become oriented at $\sim 12^\circ$ to the $ab$ plane (i.e., a $z$ component of 0.25(5) $\mu_B$) and $R_{wp}$ is reduced by 0.04 %, but this improvement cannot be regarded as significant from our data.

Analysis using ISODISTORT [14] suggests that the magnetic structure of Ce$_2$O$_2$FeSe$_2$ can be described by the C-centered space group $C2/c$ [BNS: 15.9 with basis (0, -1, 1), (-1, 0, 0), (0, 2, 0) and origin at (0, 0, 0)] shown...
in Figure 1 and refinement using 4 K data gives moments of 3.14(8) \( \mu_B \) and 1.14(4) \( \mu_B \) for Fe and Ce sites, respectively. The ordered Fe\(^{2+} \) moment in Ce\(_2\)O\(_2\)FeSe\(_2\) is comparable with that reported for the Mott insulating oxyselenides (e.g., La\(_2\)O\(_2\)Fe\(_2\)O\(_{3.4}\) \( \mu_B \)) \[19\] and the parent phase to superconducting K\(_{0.8}\)Fe\(_{1.6}\)Se\(_2\) (3.31 \( \mu_B \)) \[21\], and is consistent with a high-spin \( d^8 \) configuration for Fe\(^{2+} \) sites. It is significantly larger than that observed in LnFe\(_2\)O\(_5\) materials with poor metallic behavior (e.g., 0.94(3) \( \mu_B \) for CeFe\(_2\)O\(_5\) at 1.7 K \[25\]).

The sequential Rietveld refinements using NPD data collected on cooling show that the Ce moment increases almost linearly at low temperatures. The Fe moment can be fitted well by the critical behavior with \( \beta = 0.28(1) \) and \( T_N = 175.8(8) \) K (Fig.3) for 100 K < \( T < 171 \) K. This Fe\(^{2+} \) moment ordering is similar to that observed for CeFeAsO at \( T_N = 137 \) K, which can be described by critical behavior with \( \beta = 0.24(1) \) \[30\]. These values for \( \beta \) are larger than those reported for 2D-Ising like systems (including undoped BaFe\(_2\)As\(_2\) (\( \beta = 0.125 \) \[50\]) and La\(_2\)O\(_2\)Fe\(_2\)O\(_{3.9}\) (\( \beta = 0.122 \) \[19\])), but smaller than those predicted for three-dimensional critical fluctuations (\( \beta = 0.326 \), 0.367 and 0.345 for 3D Ising, 3D Heisenberg and 3D XY systems, respectively) \[31\]. The crossover between 2D and 3D universality classes has been suggested to originate from a coupling to an orbital degree of freedom \[52\] or the proximity of a Lifshitz point (see, for example, Fe\(_{1+x}\)Te \[53\] and BaFe\(_2\)As\(_2\) \[54\]).

The unusual change in the relative intensities of the different magnetic Bragg reflections observed on cooling Ce\(_2\)O\(_2\)FeSe\(_2\) (Fig.2) can be rationalised in terms of the contribution of the Ce and Fe moments to peak intensities. The magnetic modes that describe the ordering of both the Fe and Ce moments have the same basis vector \( \vec{k} = (0 \frac{1}{2} \frac{1}{2}) \). As a consequence, the ordering on these two sublattices contributes to mostly the same reflections. Based on the magnetic unit cell \( a_n \times 2b_n \times 2c_n \), the hkl reflections with \( h = 2n, k, l \neq 2n \) and \( h+k+l = 2n \) (i.e., \( (0 \ 1 \ 1), (0 \ 1 \ 3), (0 \ 1 \ 5) \)) have contributions from both Ce and Fe sublattices, whilst some weaker hkl reflections with \( h \neq 2n, k, l \neq 2n \) and \( h+k+l \neq 2n \) have contributions only from the Ce ordering. The ordering of the Fe and Ce sublattices adds constructively for some peak intensities (e.g., \( (0 \ 1 \ 1), (0 \ 1 \ 9) \)) and destructively for others (e.g., \( (0 \ 1 \ 5), (0 \ 1 \ 7), (0 \ 1 \ 3) \)). For this latter \((0 \ 1 \ 3)\) reflection the Ce contribution is small and so the intensity is dominated by Fe ordering. The non-monotonic temperature dependence of the magnetic reflection intensities
observed for Ce$_2$O$_2$FeSe$_2$ is similar to those reported for 
Ln$_2$CuO$_4$ (Ln = Pr, Nd, $T_{N,Cu} = 250-325$ K) [50] and 
for CeVO$_3$ ($T_N = 124-136$ K) [56, 57].

B. Inelastic neutron scattering

INS was used to obtain experimental estimates for the 
magnetic exchange interactions. Low-energy fluctuations 
were studied to probe directly the Fe-Fe exchange along 
the chains. Ce crystal electric field (CEF) excitations 
were then investigated to determine the Fe-Ce exchange.

Before discussing the scattering response from 
magnetic ions, we first describe how the background was 
subtracted from the powder averaged data. The measured 
neutron scattering intensity $I_{meas}$ is proportional to the 
structure factor $S(Q, E)$ but also includes a temperature-

dependence (Figure 4) which we subtracted to determine 
the purely magnetic scattering. The temperature-dependence of 
this excitation is also different from that of the Ce$^{3+}$ CEF 
excitation: at 4 K, it has a gap of $\sim 9$ meV, which decreases on 
softening into the elastic line by 115 K (Figure 4, c). Based 
on these observations, we conclude that the low energy, 
low-$Q$ scattering originates from the Fe$^{2+}$ magnetic 
sublattice.

To separate the Ce CEF excitations from the Fe$^{2+}$ 
magnetic excitations, the CEF contribution was estimated 
by taking a cut over the momentum transfer range of $Q = 2.8 - 3.5$ Å$^{-1}$, and then scaling by the Ce$^{3+}$ form 

factor [62] to estimate the momentum dependence. This 
subtraction takes advantage of the fact that the crystal 
field excitations are dispersionless and flat in momentum 
transfer, particularly in comparison with the strong 
momentum dependence of the scattering associated with the 
Fe sites (as observed for La$_2$O$_2$Fe$_2$OSe$_2$ [19] for example). 
This analysis leaves only the strongly momentum 


trying component near $Q = 0$ (Figure 4), from which 
the magnetic exchange interactions between Fe$^{2+}$ sites 
can be estimated.

The single-mode approximation [63] can be used to 
compare possible magnetic structures with different signs 
(AMF $J_1 < 0$, FM $J_1 > 0$) and magnitudes for the nn 
interaction $J_1$ (illustrated in Figure 6). Using the single 

mode approximation the structure factor $S(Q, E)$ can be 
written in terms of a momentum-dependent term $S(\vec{Q})$ 
and a single Dirac delta function in energy:

$$S(\vec{Q}, E) = S(\vec{Q})\delta[E - \epsilon(\vec{Q})].$$ (1)

where $\epsilon(\vec{Q})$ is the dispersion. We approximate $\delta(E)$ as 
a Lorentzian term with full-width equal to the calculated 

resolution width in energy. The first moment sum rule [64] relates $S(\vec{Q})$ to the dispersion:

$$S(\vec{Q}) = -\frac{2}{3} \frac{1}{\epsilon(\vec{Q})} \sum_\vec{d} J_1 (\vec{S}_0 \cdot \vec{S}_d) [1 - \cos(\vec{Q} \cdot \vec{d})].$$ (2)

where $\vec{d}$ is the bond vector connecting nn spins with an 
exchange interaction $J_1$. Making the assumption that 
this intrachain interaction dominates, we use the 

dispersion relation for the one-dimensional (1D) chain system:

$$\epsilon(\vec{Q})^2 = 4S^2(\Delta^2 + J_1^2[1 - \cos(\pi H)]^2).$$ (3)

where $\Delta$ is the gap value determined by anisotropy and 
$J_1$ is the nn intrachain exchange interaction.

Representative calculations using the AFM and FM 
chain models are summarized in Figure 4. The AFM 
model gives correlations at finite $Q$, whereas the FM 
model gives magnetic scattering only at lowest measurable 

wave vectors (near $Q = 0$). From the temperature 
dependence (Figure 4, c) and the subtracted data (Figure 
4, h), the strongly temperature dependent magnetic 
scattering is present near $Q = 0$. This is more consistent 
with a dominant FM $J_1$ interaction (simulated in 
Figure 4, h) than an AFM interaction where the scattering 
is peaked at finite $Q$. Based on this comparison, we 
conclude that the exchange mechanism is predominately 
ferromagnetic ($J_1 > 0$), consistent with analysis of NPD 
data described above. Figure 4, f shows results of single 
mode calculations for this FM chain model for various
FIG. 4. [color online] MARI scan with $E_i = 40$ meV showing Ce CEF excitation and magnetic excitation from the Fe sublattice at (a) 4 K, (b) 75 K and (c) 115 K. (d) MARI scan with $E_i = 40$ meV with scattering due to Ce CEF subtracted (see text) showing only magnetic excitation from the Fe sublattice. Powder averaged single mode analysis spin wave calculations with (e) AFM and (f) FM chains along [100]. An intrachain exchange interaction $J_i = 10$ meV (positive sign denotes FM interactions) was used in these spin-wave calculations. (g), (h) show single mode calculations for different magnitudes of the FM $J_i$ interaction. (The white regions at lowest momentum transfer are masked by the beam stop, and the curvature with increasing energy transfer of this inaccessible region is due to the fixed incident energy kinematics imposed by the instrument geometry.)

values of $J_1$. It is difficult to give an accurate value for this exchange interaction given the scattering is concentrated near $Q = 0$, but our calculations indicate that $J_1 \sim 10-20$ meV gives the best qualitative agreement with the observed data. It should be emphasized that this is an estimate of the coupling and is limited by the kinematics of the scattering geometry described above.

Having discussed the Fe-Fe exchange, we now discuss the localized Ce$^{3+}$ CEF excitations observed in the INS data at $\sim 11$ meV and $\sim 37$ meV (Fig. 5) with the goal of extracting the coupling between Fe and Ce sites. The magnetic nature of the peak around 11 meV is confirmed by the temperature dependence shown in Figure 5. The softening of the first crystal field excitation (Fig. 5a-f) with increasing temperature could be the result of thermal expansion or of a change in the ground state [65]. We note that the softening observed can be reproduced by point charge calculations and is consistent with thermal expansion. To obtain an estimate of Fe – Ce exchange, it is important to have a heuristic model for the Ce crystal fields from which eigenfunctions and transition energies can be derived. Ce$^{3+}$ ($4f^1$, $J = \frac{5}{2}$) is a Kramers ion (Fig. 5), and each level remains doubly degenerate for all crystalline electric fields unless a magnetic field is applied. Magnetic ordering on the iron sublattice can give rise to a molecular field at the Ce$^{3+}$ sites if there is coupling between Fe$^{2+}$ and Ce$^{3+}$ ions. In the oxyarsenide CeFeAsO, the degeneracy of Ce$^{3+}$ CEF states is lifted below $T_{N,Fe}$ suggesting some Fe - Ce coupling [66], which is consistent with muon spin rotation spectroscopy studies [30]. In the vacancy-ordered Ce$_2$O$_2$FeSe$_2$ structure (space group Ima$\overline{3}$), the Ce atoms are on 8j sites with local point symmetry $C_2$. The resulting crystal field Hamiltonian can be expressed in Stevens operators formalism which requires five nonzero terms to describe the monoclinic symmetry of the Ce$^{3+}$ site [67]:

\begin{equation}
H = \sum_{\alpha} \epsilon_{\alpha} \Omega_{\alpha} + \sum_{\alpha,\beta} g_{\alpha,\beta} \Omega_{\alpha} \Omega_{\beta}
\end{equation}
We now use this heuristic model of the crystal fields to derive an exchange coupling between the Fe – Ce ions based upon the broadening of the crystal field levels in the magnetically ordered low temperature phase. Because of Kramer’s theorem, the crystal field excitations are doubly degenerate and only split in the presence of a time reversal violating magnetic field. This splitting can be calculated by adding the following Zeeman term to the crystal field Hamiltonian above for eigenstates $i$ and $j$:

$$H_{\text{Zeeman}(i,j)} = \mu_0 \mu_B H \langle i | J_z | j \rangle$$

where $\mu_B$ and $\mu_0$ are the Bohr magneton and permeability of free space, respectively, $H$ is the effective magnetic field, $J_z$ is an angular momentum operator along $z$, and $\langle i | J_z | j \rangle$ is the angular momentum matrix element from the ground state to the excited state. To account for the powder averaging, all three directions ($x$, $y$, and $z$) were averaged. The molecular field on the Ce site is induced by magnetic ordering on the Fe sublattice. In the absence of a molecular field at the Ce sites, any splitting/broadening of the Kramers doublets should arise from the Fe – Ce coupling [66] and is consistent with muon spin relaxation studies, which indicate a strong non-Heisenberg anisotropic Fe – Ce exchange well above $T_{N,\text{Ce}}$ in CeFeAsO [40]. In the Fe-ordered crystal structure of Ce$_2$O$_2$FeSe$_2$ (Fig.1), the FM chains of edge-shared FeSe$_4$ tetrahedra alternate with vacant stripes along [010] and each Ce site is coupled to two Fe sites within a single FM chain (Fig.1) and there are no competing Fe – Ce interactions. The molecular field on the Ce site due to the Fe magnetic sublattice is equal to $2 SJ_4$ where $J_4$ is the Fe – Ce exchange coupling. This provides an opportunity to probe the Fe – Ce coupling by measuring the broadening of the crystal field excitations.

The CEF levels observed for Ce$_2$O$_2$FeSe$_2$ are broadened (Fig.5d–f) considerably beyond the instrumental resolution (represented by the horizontal bar in Fig.5c), but it is difficult to determine the splitting of the Kramers doublets (Fig.5b) in contrast to the case of CeAsFeO. To provide an estimate for the Fe – Ce exchange coupling, we have fitted the low temperature excitation to a single Gaussian to obtain a full-width of 2.0(4) meV, giving a maximum value for any splitting of $\sim$1 meV. Using the Stevens parameters discussed above for the crystal field analysis, we obtain an estimate of the Fe – Ce exchange $J_4$ of $\sim$0.15 meV. This estimate is approximately an order of magnitude smaller than the ferromagnetic Fe – Fe exchange $J_1$ interaction discussed above.

### C. Spin exchange and electronic structure

Summarizing the experimental results above, we observe ferromagnetic Fe – Fe and weaker ferromagnetic
we consider five ordered spin states FM and AF1 – AF4 employed to extract them with previous calculations. The goal of understanding these results and comparing the structure observed experimentally from diffraction with a weak J4 exchange expected from neutron inelastic scattering.

Fe – Ce exchange. This is based on both magnetic neutron diffraction and inelastic scattering results. In this section, we provide electronic structure calculations with the goal of understanding these results and comparing them with previous calculations.

Figure 6 shows the four spin exchanges of Ce2O2FeSe2 we investigate, namely, the intrachain exchange, J1, and the interchain exchanges, J2 and J3, between Fe2+ ions as well as the exchange J4 between Fe2+ and Ce3+ ions. To extract the values of J1 – J4 by energy-mapping analysis [68][70], we consider five ordered spin states FM and AF1 – AF4 presented in Figure 6a-f. The FM, AF1 and AF2 states contain FM chains. The coupling between adjacent FM chains is FM in the FM and AF1 states, but AFM in the AF2 state. The coupling between the Fe2+ and Ce3+ ions is FM in the FM and AF2 states, but AFM in the AF1 state. The AF3 and AF4 states consist of AFM chains so that the net spin exchange between the Fe2+ and Ce3+ ions vanishes. The coupling between adjacent AFM chains is FM in the AF3 state, but AFM in the AF4 state. The AF2 state is closest to that observed experimentally. The total spin exchange energies of the FM and AF1 – AF4 states can be expressed in terms of the spin Hamiltonian,

$$H = - \sum_{i<j} J_{ij} \vec{S}_i \cdot \vec{S}_j. \quad (7)$$

where Jij = J1 – J4 is the spin exchange parameter for the interaction between the spin sites i and j. By applying the energy expression obtained for spin dimers with N unpaired spins per spin site (four for Fe2+, and one for Ce3+) [71, 72], the total spin exchange energies per formula unit (FU) of the FM and AF1 – AF4 states can be written as

$$E = (n_1 J_1 + n_2 J_2 + n_3 J_3) \left( \frac{N_F^2}{4} \right) + ... + n_4 J_4 \left( \frac{N_F N_C}{4} \right), \quad (8)$$

where NF = 4 and NC = 1, and the coefficients n1 – n4 for the five spin ordered states are summarized in Figure 6a-f. We examined the relative energies of the FM and AF1 – AF4 states on the basis of DFT+U electronic structure calculations with various UFe and UCe values. From their DFT+U calculations, Li et al. [73] found that the experimentally reported magnetic structure (namely, the AF2 state) is stable for UCe = 12 eV with UFe = 0. Our calculations show that structures with FM chains (AF1 and AF2) are significantly more stable than those with AFM chains (AF3 and AF4) for all combinations of UFe and UCe given here (Table I) (for UFe > 2 eV, the nn Fe – Se – Fe spin exchange J1 becomes AFM). AF1 and AF2 spin arrangements differ in the sign of Fe – Ce exchange J4: in AF1, Ce spins are antiparallel to nn Fe spins (i.e., AFM J4 exchange), whereas Ce spins are parallel to nn Fe spins (i.e., FM J4) in the AF2 arrangement. We note that the experimentally observed AF2 arrangement is the more energetically favourable for all UFe and UCe combinations considered, but that the relative stability of AF2 over AF1 is much greater with UCe = 12 eV than with UCe = 10 eV.

### Table I. Energies (in meV per formula unit) of AF spin arrangements shown in Figure 6 relative to FM arrangement for various UFe and UCe values (in eV).

|     | AF1 | AF2 | AF3 | AF4 |
|-----|-----|-----|-----|-----|
| UFe = 2, UCe = 12 | +1.2 | -33.0 | +149.5 | +150.8 |
| UFe = 2, UCe = 10 | -4.9 | -9.7 | +139.1 | +178.1 |
| UFe = 0, UCe = 12 | +0.1 | -35.0 | +167.5 | +169.0 |
| UFe = 0, UCe = 10 | 0.0  | -5.9 | +218.1 | +222.1 |

By mapping the relative energies of the FM and AF1 – AF4 states, determined from the DFT+U calculations with UFe = 2 eV and UCe = 12 eV (see Fig. 6a-f), onto the corresponding relative energies determined from Eq. 8, we obtain J1 = 21.3 meV, J2 = -1.4 meV, J3 = -1.4 meV, and J4 = 0.2 meV (see Table I). These spin exchanges are consistent with the observed magnetic structure of Ce2O2FeSe2. The calculated value for the Fe – Se – Fe exchange, J1 ~ 21 meV, is comparable in magnitude to the experimental value of about 10 – 20 meV from
INS. Furthermore, the calculated value for the Fe – Ce exchange, \( J_4 = 0.2 \) meV, is in good agreement with the experimental value of about 0.15 meV. Similar energy-mapping analyses were carried out with other values of \( U_{Fe} \) and \( U_{Ce} \), as shown in Table [II]. These calculations show that \( J_1 \) is strongly FM and that \( J_4 \) is weakly FM for the \( U_{Fe} = 2 \) eV and \( U_{Ce} = 12 \) eV combination (all other combinations give \( J_4 \) weakly AFM).

| \( U_{Fe} = 2, U_{Ce} = 12 \) | \( J_1 \) | \( J_2 \) | \( J_3 \) | \( J_4 \) |
|------------------------|--------|--------|--------|--------|
| \( J_1 = 21.3 \) | +1.4   | +1.4   | +0.2   |
| \( J_2 = 10 \)    | +20.7  | +1.8   | -1.5   | -0.6   |
| \( J_3 = 12 \)    | +23.2  | -2.1   | -1.1   | +0.0   |
| \( J_4 = 10 \)    | +27.9  | -0.1   | -0.3   | 0.0    |

Figure 2 shows plots of the projected density of states (PDOS) obtained for the Ce 4f, Ce 5d, Fe 3d and Se 4p states of CeO2FeSe2 from the DFT+U calculations with \( U_{Fe} = 2 \) eV and \( U_{Ce} = 6, 8, 10 \) and 12 eV. It shows a band gap of about 1 eV which is consistent with the semiconducting behavior of CeO2FeSe2 observed experimentally (with band gap of 0.64 eV). [34]

We note from Figure 7 that the Fe 3d states overlap with the Se 4p states throughout the filled energy region, which indicates that the interaction between Fe 3d and Se 4p orbitals takes place throughout this energy range. The Ce 5d states contribute to the filled region of the Fe 3d and Se 4p states, and these contributions are not strongly affected by the change in \( U_{Ce} \). However, on increasing \( U_{Ce} \) from 6 eV to 12 eV, the Ce 4f states are gradually lowered in energy such that they overlap with the filled Fe 3d and Se 4p states when \( U_{Ce} < 12 \) eV, but not when \( U_{Ce} \geq 12 \) eV. Likewise, the filled Ce 4f states overlap with the Ce 5d states when \( U_{Ce} < 12 \) eV but do not when \( U_{Ce} \geq 12 \) eV. The ferromagnetic Fe – Se – Ce spin exchange \( J_4 \) (and increased stability of the experimentally observed AF2 spin arrangement) is found when the Ce 5d states do not overlap in energy with the Fe 3d and Se 4p states in the energy region within 2 eV below the Fermi level. This is understandable because an antiferromagnetic Fe-Se-Ce spin exchange would involve the Fe 3d, Se 4p and Ce 5d orbitals. That the electronic structure of CeO2FeSe2 is described by using a small value of \( U_{Fe} \) (2 eV) suggests a weakly correlated nature of the iron-selenide sheets in CeO2FeSe2. This is similar to that found for parent materials to iron-based superconductors (\( U_{Fe} \sim 2 \) eV for SmFeAsO and BaFe2As2 [47] and \( \sim 4 \) eV used to describe the electronic properties of K0.76Fe1.72Se2 [75]. The need for a large on-site repulsion \( U_{Ce} \) for Ce (12 eV) is comparable to the trend established for CeFeAsO where \( U_{Ce} = 9 \) eV was required [76].

4. DISCUSSION

In the low-temperature magnetic structure of CeO2FeSe2, both Ce\(^{3+}\) and Fe\(^{2+}\) moments lie within the ab plane, similar to the structure reported for CeFeAsO [25]. The observation of in-plane Ce\(^{3+}\) moments is consistent with the easy-axis along x proposed for Ce\(^{3+}\) sites in orthorhombic CeFeAsO [77]. The ordered Ce\(^{3+}\) moment of CeO2FeSe2 at 4 K (1.14(4) \( \mu_B \)) is slightly larger than that reported for CeFeAsO (0.83(2) \( \mu_B \) at 1.7 K) [25], and is close to that expected for a Ce\(^{3+}\) doublet ground state (1 \( \mu_B \)) [69]. The high ordering temperature for the Ce moments implied by our NPD data is surprising; other systems known to have high Ce ordering temperatures include CeRh12B2 (115 K) in which Ce\(^{3+}\) ion is the only magnetic ion [78] and CeVO3 (50 K) in which Ce ordering is thought to arise from FM exchange between Ce\(^{3+}\) and V\(^{3+}\) ions [56, 57]. The high Ce\(^{3+}\) moment ordering temperature in CeO2FeSe2 is most probably due to the FM spin exchange between adjacent Ce\(^{3+}\) and Fe\(^{2+}\) ions, that is, the long range magnetic order of the Fe\(^{2+}\) sublattice induces that of the Ce\(^{3+}\) ions. In CeFeAsO, each Ce site is coupled to two FM chains of edge-sharing FeAs tetrahedra with opposite spin orientations [25], leading to frustration of any Ce – Fe exchange interactions [23]. This is expected to give a negligible field on the Ce site (consistent with the low Ce moment ordering temperature). The very small CEF splitting (\( \sim 1 \) meV) observed for CeO2FeSe2 is similar to that described for the parasitic ordering of Ce\(^{3+}\) moments in CeMnAsO [80].

The nn Fe – Fe magnetic exchange interactions, \( J_1 \), determined here experimentally are in good agreement with our DFT calculations. They are similar in magnitude to those reported for CeFeAsO [61] but of opposite sign. They are significantly larger than those reported for La2O2FeOSe2, in which the Fe\(^{2+}\) cations are coordinated by both oxide and selenide anions, which may give rise to more strongly correlated behavior [49]. We note that the nn \( J_1 \) interactions in CeO2FeSe2 are FM, which may reflect some orbital ordering on Fe sites, as proposed for the pnictides [62].

5. CONCLUSIONS

In conclusion, the FM nature of Fe – Se – Fe nn interactions \( J_1 \) has been confirmed by NPD and INS measurements. INS work indicates that this exchange is \( \sim 10 \) – 20 meV. This is consistent with DFT + U calculations for \( U_{Fe} \leq 2 \) eV and suggest that the Fe 3d electrons in the Fe0.5Se sheets in CeO2FeSe2 are weakly correlated, sim-
**APPENDIX A: INS DATA ANALYSIS**

The principle of detailed balance can be used to estimate the temperature-independent background contribution to the scattering. We can approximate that for a fixed wave vector and energy transfer, the neutron energy gain (negative energy transfer, $(-|E|)$) and neutron energy loss (positive energy transfer, $(+|E|)$) are related by the following expression from the detailed balance principle:

\[
I_{\text{meas}}(+|E|,T) = B_1(|E|) + S(|E|,T) \quad (A1)
\]

\[
I_{\text{meas}}(|E|,T) = B_2(|E|) + S(|E|,T) e^{-|E|/k_BT} \quad (A2)
\]

where $B_1$ and $B_2$ are temperature-independent background points, $S(|E|,T)$ is the scattered intensity (with both magnetic and phonon contributions) and $e^{-|E|/k_BT}$ is the Boltzmann factor. We assume that the resolution of the inelastic scattering does not change over the energy range investigated. With data collected at two or more temperatures, $B_1$ and $B_2$ can be determined. For $E_i = 40$ meV, data were collected at six temperatures (4 K, 75 K, 115 K, 150 K, 200 K and 300 K). These data give us experimental data points in both the energy gain and energy loss spectra (giving 12 data points in total).
with which the two background points $B_1$ and $B_2$ and the six values for $S(E, Q, T)$ can be determined.

This detailed balance allows us to isolate the inelastic scattering but this has contributions from both magnetic and phonon scattering. The measured intensity $I_{\text{meas}}$ is proportional to the structure factor $S(Q, E)$ which is related to the imaginary part of the susceptibility $\chi''(Q, E)$:

$$I_{\text{meas}} \propto S(Q, E) = \frac{1}{\pi} \left[ n(E) + 1 \right] \chi''(Q, E) \quad (A3)$$

where $n(E)$ is the Bose factor. The scattering at 300 K is dominated by phonons and so the phonon contribution $\chi''_{\text{phonon}}(Q, E)$ can be written:

$$\chi''_{\text{phonon}}(Q, E) = \frac{S_{300K}(Q, E)}{[n(E)_{300K} + 1]} \quad (A4)$$

The phonon contribution at each temperature was then estimated using equation A3 and subtracted to obtain the purely magnetic scattering at each temperature.

**APPENDIX B: POINT CHARGE CLUSTER MODEL CALCULATION**

To guide the CEF analysis, we used a point charge “cluster” model (integrated over 40 unit cells to ensure convergence of the Stevens coefficients) which gave the results shown in Table B1.

| Stevens coefficients value (meV) | $B_2^0$ | $B_2^2$ | $B_3^0$ | $B_3^2$ | $B_4^0$ |
|---------------------------------|--------|--------|--------|--------|--------|
| $B_2^0$                         | 10.13  |        |        |        |        |
| $B_2^2$                         | 0.0039 |        |        |        |        |
| $B_3^0$                         | -0.10  |        |        |        |        |
| $B_3^2$                         | -0.0021|        |        |        |        |
| $B_4^0$                         | -0.60  |        |        |        |        |

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