A RIXS investigation of the crystal-field splitting of Sm$^{3+}$ in SmB$_6$

Andrea Amorese,1,2 Oliver Stockert,2 Kurt Kummer,3 Nicholas B. Brookes,3 Dae-Jeong Kim,4 Zachary Fisk,4 Maurits W. Haverkort,5 Peter Thalmeier,2 Liu Hao Tjeng,2 and Andrea Severing1,2

1Institute of Physics II, University of Cologne, Zülpicher Straße 77, 50937 Cologne, Germany
2Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, 01187 Dresden, Germany
3European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS40220, F-38043 Grenoble Cedex 9, France
4Department of Physics and Astronomy, University of California, Irvine, CA 92697, USA
5Institute for Theoretical Physics, Heidelberg University, Philosophenweg 19, 69120 Heidelberg, Germany

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The crystal-field (CF) splitting of the $^6H_{5/2}$ Hund’s rule ground state of Sm$^{3+}$ in the strongly correlated topological insulator SmB$_6$ has been determined with high resolution resonant inelastic x-ray scattering (RIXS) at the Sm M$_2$ edge. The valence selectivity of RIXS allows isolating the crystal-field-split excited multiplets of the Sm$^{3+}$ ($4f^6$) configuration from those of Sm$^{2+}$ ($4f^5$) in intermediate valent SmB$_6$. The very large energy range of RIXS allows the crystal-field analysis of a high lying multiplet at about 2.4 eV that has the same total angular momentum $J$ as the ground state so that ambiguities due to the elastic tail can be avoided. We find that the $\Gamma_7$ doublet and $\Gamma_5$ quartet of the $^6H_{5/2}$ Hund’s rule ground state are split by $\Delta^{\text{CF}}_{^6H_{5/2}} = 20\pm 10\text{ meV}$ which sets an upper limit for the $4f$ band width. This indicates an extremely large mass renormalization from the band structure point, pointing out the need to consider the coefficients of fractional parentage for the hopping of the $4f$ electrons.

SmB$_6$ is an intermediate valent Kondo insulator in which the hybridization of localized 4$f$ electrons and the conduction band (cf-hybridization) leads to the formation of a gap $\Delta_h$ [1–5] of the order of 20 meV [6–11]. Accordingly, the resistivity increases with decreasing temperature but instead of diverging it reaches a plateau below about 10 K. Surface states could be an explanation for this, the cubic CF splitting of the $\Gamma_8$ states is spherical [42]. In contrast, the cubic CF splitting of the $\Gamma_8$ quartet and $\Gamma_7$ doublet of the lowest energy multiplet $^6H_{5/2}$ of Sm$^{3+}$ 4$f^5$ has eluded its determination till today.

Band structure calculations have been very successful in the field of semiconducting topological insulators, but they are not adequate for the rare earths because of correlations, nor are they accurate enough because the energy scales are much smaller. For example, several density functional theory calculations imply that the hole of the $4f^5$ configuration resides in the doublet $\Gamma_7$ [22, 43–46] but a recent hard x-ray non-resonant inelastic x-ray scattering (NIXS) investigation [47, 48] by some of the authors of the present study reveals that the ground-state symmetry of the Sm$^{3+}$ configuration is the $\Gamma_8$ quartet. Band structure calculations also suggest energy scales of the order of hundred meV for $\Delta^{\text{CF}}_{^6H_{5/2}}$ (see e.g. [45, 46]) although the extrapolation of the CF parameters within the REB$_6$ series suggests a splitting of the order of 15 meV; an extrapolation that is, of course, only valid in diluted systems [49, 50]. Along the same line, band structure calculations produce $4f$ band widths of several hundred meV, while so far no $4f$ dispersions in ARPES have been observed within the experimental resolution [6–11, 24–28]. The inclusion of correlation effects using Gutzwiller or dynamical mean field approaches (DMFT) [22, 51] does produce narrower bands and smaller CF splittings but it is not clear whether the mass renormalizations used or found are realistic.

Inelastic neutron scattering (INS) is the obvious technique for tackling this problem, but although providing very useful information on SmB$_6$, INS has not been successful in finding $\Delta^{\text{CF}}_{^6H_{5/2}}$. The strong neutron absorption of Sm and B even in double isotopic samples, the superposition of both Sm configurations, and the presence of cf-hybridization cause serious complications. Nevertheless, the following pieces of information have been obtained by INS: The spin orbit transitions $^7F_0 \rightarrow ^7F_1$ and $^6H_{5/2} \rightarrow ^6H_{7/2}$ at $\approx 35$ meV and $\approx 130$ meV have been ob-
FIG. 1. (color online) a) RIXS process at the Sm $M_5$-edge ($3d \rightarrow 4f$) from an intermediate valent ground state of the two Sm configurations $4f^6$ (red) and $4f^5$ (blue) - see text. Inset: experimental, bulk sensitive fluorescence-yield x-ray absorption spectrum (FY-XAS) of Sm $M_5$-edge of SmB$_6$ (black circles), the XAS simulation (gray line) decomposed into 60% Sm$^{3+}$ (blue line) and 40% Sm$^{2+}$ (red line) spectral weights according to [36-40], plus the XAS simulation including self-absorption (brown line) [41]. For graphical clarity the XAS simulations are scaled down by a factor of three. The colored dots $A$, $B$, and $C$ resemble the incident energies $\hbar \omega_{\text{in}}$ used in the RIXS experiment. b) Calculated RIXS spectra ($\hbar \omega_{\text{in}} - \hbar \omega_{\text{out}}$) of both Sm valence states (Sm$^{2+}$ red [$\hbar \omega_{\text{in}} = B$], Sm$^{3+}$ blue [$\hbar \omega_{\text{in}} = C$]) for the geometry shown in Figure 3(a) and vertical ($\sigma$) polarization of the incident photons. The red, blue, and green boxes next to the RIXS spectra show energy levels on expanded scales so that multiplet as well as expected crystal-field splittings are resolved. Thicker lines stand for higher degeneracies. The splitting $\Delta^G_{3/2}$ (green box) is used for determining $\Delta^F_{\text{in} 3/2}$ (blue box).

served [52, 53] (see near-ground state multiplets in red and blue boxes of Fig.1(b)). At low temperatures a long living spin resonance at about 14 meV shows up in the poly- and single crystalline data [52, 53] at the X and $R$ high symmetry points with a form factor that is not 4f-like [54]. More recent INS data show that the spin resonance with an intrinsic width of about 0.1 meV (FWHM) decays above 30 K and that at low temperatures no magnetic intensity is observed below the energy of this resonance which is typical for a spin gap [55]. At 100 K i.e. well above the temperature at which the many body spin resonance disappears, quasielastic magnetic intensity ($\Gamma/2 \approx 10$ meV HWHM) following the Sm$^{3+}$ magnetic form factor has been extracted by Alekseev et al. after a very careful intensity examination [56]. This is suggestive of the recovery of the single ion, though broadened, magnetic spectrum, but the size the CF splitting of the Sm$^{3+}$ Hund’s rule ground state remains undetermined. We note that also the high resolution ARPES studies so far have not been able to detect the CF splitting, unlike in for example YbIr$_2$Si$_2$ [57], which maybe due to the complications of the SmB$_6$ surface [7, 30, 31].

Here resonant inelastic x-ray scattering (RIXS) is a promising option [58, 59]. RIXS is not only element, it is also configuration selective. This is well known from studying valences at the rare earth L-edge in the so called partial fluorescence yield mode [60, 61]. Here we use the configuration selectivity at the $M_{1,5}$-edge ($3d \rightarrow 4f$) to distinguish the excitation spectra of the two Sm configurations.

Figure 1 shows the $M_5$-edge RIXS process for SmB$_6$. The initial state configuration is an admixture of Sm$^{3+}$: $3d^{10}4f^6$ (red) and Sm$^{3+}$: $3d^{10}4f^5$ (blue). The resonant absorption of an ≈1090 eV x-ray photon at the $M_5$ edge ($3d_{5/2} \rightarrow 4f$) creates a core hole. In this intermediate state the absorption lines of the two configurations are split in energy due to the different impact of the core hole potential on either configuration. Finally, in RIXS spectroscopy the intensity of the photons emitted by the resonant radiative decay is monitored as a function of the outgoing photon energy ($\hbar \omega_{\text{out}}$) so that energy transfer spectra can be measured. In principle the decay process in the RIXS process of SmB$_6$ yields the superposition of two multiplet spectra (see simulations of two independent configurations in Fig. 1(b)) but the choice of the incident photon energy $\hbar \omega_{\text{in}}$ along the XAS edge allows enhancing the signal of one of the two configurations. It is possible to resolve the CF splittings in a RIXS experiment because the large life time broadening of the intermediate state does not enter, i.e. the life time broadening in RIXS that
matters is that of the final state [62–65].

Figure 1(b) shows calculation of RIXS spectra for pure Sm$^{2+}$ (red) and pure Sm$^{3+}$ (blue). The photon-in photon-out RIXS process yields the selection rule $\Delta J = 0, \pm 1, \pm 2$ so that multiplets with $J = 0, 1, 2$ (for Sm$^{2+}$) and $J = 1/2, 3/2, 5/2, 7/2$, and $9/2$ (for Sm$^{3+}$) are accessible, the latter ones being so weak that they are not shown. In the cubic point symmetry of SmB$_6$ only multiplets with $J \geq 2$ are CF split as shown on an enlarged energy scale in the colored boxes of Fig. 1(b).

Apart from the valence selectivity, another advantage of RIXS is that the transferred energy is, in contrast to INS, practically unlimited, i.e. with RIXS we can study higher lying multiplets instead of the strongly hybridized Hund’s rule ground state of Sm$^{3+}$ (blue box in Fig. 1(b)). We will show that we can take advantage of the CF effect on the $^4G_{5/2}$ multiplet at about 2.4 eV (see the green box in Fig. 1(b)). The asterisk indicates that due to the particularly strong intermultiplet mixing acting on this level, $L$ is no longer a good quantum number so that the multiplet labeling is not strictly valid. The total angular momentum $J = 5/2$, however, remains a good quantum number for CF splittings smaller than the SO splittings. $^4G_{5/2}$ and the Hund’s rule ground state $^6H_{5/2}$ have the same $J$ so that the same CF parameter $A^2_{ij}$ [66] (together with $A^1_{ij} = \sqrt{5/14}A^0_{ij}$) determines the CF splitting. The size of the splitting is given by $A^2_{ij}\tilde{\beta}_{JLS}$ whereby $\tilde{\beta}_{JLS}$ is something like a Stevens factor that is calculated within the full multiplet routine, while $A^2_{ij}$ is determined experimentally. Hence, we can gain information on the splitting of the lowest energy $^6H_{5/2}$ multiplet by fitting the RIXS signal of the $^4G_{5/2}$ multiplet. For $^4G_{5/2}$ the $\tilde{\beta}_{JLS}$ factor is larger than for $^6H_{5/2}$ (approximately double) so that the CF splitting is larger and less hampered by the limited energy resolution at the Sm $M_2$-edge. In addition, the signal is free of the strong tail of the elastic peak (at 0 eV) and of the signal from other low energy excitations.

The SmB$_6$ [16] $M$-edge RIXS experiment at 20 K was performed at the ERIXS spectrometer of the ID32 beamline [67] at the European Synchrotron Radiation Facility (ESRF), Grenoble, France with a resolution of 45 meV at the Sm $M_2$-edge ($\approx 1090$ meV). Data were taken with two different scattering angles, namely $2\Theta = 90^\circ$ and $150^\circ$. Further details of the set-up are given in the Appendix. Simulation were performed with the full multiplet code Quanty [68, 69]. Atomic parameters were taken from the Cowan code [70] and the reduction factor of the Slater integrals $r_{4f-4f} = r_{3d-4f} = 0.86$ were used (see Appendix). These values are in agreement with those in Ref. [47].

The inset of Fig 1(a) shows the bulk-sensitive experimental fluorescence-yield XAS (FY-XAS) data of the Sm $M_2$-edge of SmB$_6$ at 20 K, with the photon polarization parallel to the 100 direction (black line). These data have been simulated by calculating an XAS spectrum (gray line) containing Sm$^{3+}$ (40 %) and Sm$^{2+}$ (60 %) spectral weights according to the SmB$_6$ valence at low $T$ [36–40]. Then self-absorption effects were included in the simulation (see brown line) [41] and compared with the FY-XAS data. Note, for reasons of graphical clarity the XAS data have been rescaled by a factor of three. The orange, purple and green dots marked $A$, $B$, and $C$ indicate the incident energies that were used for the RIXS experiment.

Figure 2(a) shows the RIXS data at $T = 20$ K up to 3 eV taken with the three different incident energies $\hbar\omega_{in} = A, B, \text{ and } C$ and a scattering angle of $2\Theta = 90^\circ$. $\hbar\omega_{in} = A$ corresponds to the pre-edge region where the $3d \rightarrow 4f$ absorption process is dominated by the ground state of Sm$^{2+}$ $4f^6$. The asymmetric intensity close to the elastic line is indicative for the low energy transitions $^7F_0 \rightarrow ^7F_1$ at 35 meV and some $^7F_0 \rightarrow ^7F_2$ at about 150 meV, whereas higher energy transfers have no cross-section because they require larger incident energies due to selection rules. At $\hbar\omega_{in} = C$ the absorption arises mainly from the $4f^5$ ground state of Sm$^{3+}$. Energy $B$ is in-between, i.e. the RIXS spectrum shows features characteristic of both valences but is not simply the superposition of spectrum $A$ and $C$ because of the incident energy dependence of the accessible excitations. Figure 2(b), shows full multiplet RIXS calculations for the same spectrometer configuration for Sm$^{2+}$ with the incident energies $B$ (dotted red line) and $C$ (red solid line) and for Sm$^{3+}$ with incident energy $C$ (solid blue line).
We recall that the multiplet 3+ field problem of Sm

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region of the horizontal (2.4 eV energy transfer (3+

field) polarization and two different scattering an-

we also exclude this possibility as well. It turns out that peak shapes and intensity ratios of both scattering configurations are best reproduced with \( \Delta_{\text{CF}}^{\text{H}_{5/2}} = +20 \text{ meV} \).

Figure 4 shows the same RIXS data as in Fig. 3 but after subtracting a linear background. The lines represent an empirical fit with three Voigt profiles whereby the Gaussian contribution is kept fixed to the experimental resolution. The Lorentzian widths, the line positions and intensities were varied with the simplification that directional dependent NIXS data [47]. For +40 meV CF splitting the spectral shape has changed considerably for both scattering geometries so we also exclude this possibility as well. It turns out that peak shapes and intensity ratios of both scattering configurations are best reproduced with \( \Delta_{\text{CF}}^{\text{H}_{5/2}} = +20 \text{ meV} \).

Figure 4 shows the same RIXS data as in Fig. 3 but after subtracting a linear background. The lines represent an empirical fit with three Voigt profiles whereby the Gaussian contribution is kept fixed to the experimental resolution. The Lorentzian widths, the line positions and intensities were varied with the simplification that lifetime broadening and intensity of the two CF excitations are identical. The best fits yield \( \Delta_{\text{CF}}^{\text{H}_{5/2}} \approx 43 \) and \( 48 \text{ meV} \) for the \( 2\Theta = 90^\circ \) and \( 150^\circ \) scattering configurations, respectively, corresponding to a splitting of 20 and 22 meV of the ground state multiplet \( \text{H}_{5/2} \). Other trials with larger crystal-field splittings no longer reproduce the data, see Appendix. We learn from this exercise that
\( \Delta_{H_{5/2}}^{CF} \) (\( \Delta_{H_{5/2}}^{H_{5/2}} \)) should be \(<66 \text{ meV} \) (\(<30 \text{ meV} \)). Summarizing, we thus find \( \Delta_{H_{5/2}}^{CF} = 20 \pm 10 \text{ meV} \).

The present RIXS result agrees surprisingly well with the CF splitting that is expected from the extrapolation within the REB series \([49]\). The result also explains the lineshape of the lowest \( f \) state signal as measured in photoemission \([11]\); we can now propose to describe it in terms of two Lorentzian lines, one twice as strong as the other according to a \( \Gamma_8 \) quartet ground state and a \( \Gamma_7 \) excited doublet, that are about 20 meV apart. Furthermore, the present data confirm the non-resonant inelastic x-ray scattering result of SmB\(_6\) that also finds a quartet ground state \([47, 48]\).

The finding that the CF splitting is 10 meV <\( \Delta_{H_{5/2}}^{CF} \) <30 meV in combination with the NIXS result that the ground state is not a highly mixed \( \Gamma_8 \) and \( \Gamma_7 \) state \([47]\) indicates that the \( 4f \) band width is small and less than 30 meV. Considering the fact that the band width from band structure calculations is several hundred meV, we infer that the mass renormalization is extremely large. This also gives credit to the idea that coefficients of fractional parentage should be considered for removing or adding an electron from/to the lowest Sm \( f^6 \) or \( f^5 \) multiplets measured \([71]\): a reduction factor of 0.033 can be found for the \( f-f \) hopping. A Gutzwiller study uses a somewhat less strong reduction factor \([22]\), while a DMFT calculation \([51]\) found indeed the extremely narrow bands. It should be noted however, that the sign of the CF splitting and thus also its magnitude extremely narrow bands. It should be noted however, that the sign of the CF splitting and thus also its magnitude.

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The electronic configuration selectivity, the large accessible energy transfers, and the cross-section dependence on the scattering configuration in RIXS have been instrumental to observe finger prints of the CF splitting of the Sm\(^{3+}\) Hund’s rule ground state in SmB\(_6\). We find \( \Delta_{H_{5/2}}^{CF} = 20 \pm 10 \text{ meV} \) describes the data well, thereby setting limits to the \( 4f \) band width.

**APPENDIX**

**Sample and Experiment**

The RIXS experiment was performed on aluminum flux grown single crystals \([16]\) that were aligned by Laue prior to the experiment. The data were cleaved \textit{in situ} under vacuum, then transferred to the main chamber and measured at 20 K. Data were acquired for about 5 hours for each spectrum (only 3 hours for the spectrum \( B \)). The instrument 45 meV-FWHM Gaussian response function was estimated by measuring a carbon tape. The measurements were performed with horizontal polarization

\( E \) of the incident photons, two different scattering angles, \( 2\theta = 90^\circ \) and \( 2\theta = 150^\circ \), a sample angle of \( \theta = 37.3^\circ \) and with the \( b \) and \( c \) directions of the sample in the scattering plane (see inset of Fig. 3).
Simulations were performed with the full multiplet code QuanTy [68, 69]. Atomic parameters were taken from the Cowan code [70]. Figure 5 shows that the energy positions of the multiplets depend very sensitive to changes of the reduction factor \( r_{4f^{-4f}} \) of the Slater integrals so that \( r_{4f^{-4f}} \) was determined by adjusting the energy positions of the multiplet excitations. The reduction factor \( r_{3d^{-4f}} \), on the other hand, affects only slightly the relative intensities of the RIXS peaks. We find that \( r_{4f^{-4f}} = r_{3d^{-4f}} = 0.86 \) provides a very good fit of the relative RIXS intensities and line positions, and to the XAS data. These values are in agreement with those in Ref. [47].

Figure 6 shows empirical descriptions of the \( ^4F_{3/2} \) and \( ^4F_{5/2} \) multiplets with three Voigt profiles, for the \( ^4F_{3/2} \) and two for the crystal-field split \( ^4G_{5/2} \) multiplet. The Gaussian contribution was kept fixed to the instrumental resolution of 45 meV, while the Lorentzian line widths were varied. Here the constraint was imposed that the two crystal-field excitations have the same line width and also the same intensity. The position of the three lines was varied with the limitation that the separation of the crystal-field excitations was set to specific values (see panels of Fig. 6). For \( \Delta^{CF}_{G_{5/2}} = 55 \text{ meV} \) (\( \Delta^{CF}_{G_{5/2}} = 25 \text{ meV} \)) both configurations are still well described with the three Voigt profiles, for \( \Delta^{CF}_{G_{5/2}} \geq 66 \text{ meV} \) (\( \Delta^{CF}_{G_{5/2}} \geq 30 \text{ meV} \)) it is no longer possible to describe the data with the scattering angle of \( 2\theta = 150^\circ \). This shows that the crystal-field splitting of the ground state must be smaller than 30 meV.

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