Great interest in the divalent hexaborides has been generated recently by the discovery of ferromagnetism (FM) in La-doped CaB$_6$ [1] and by exotic theoretical models to explain the unusual magnetism, e.g. that it represents the ground state of a dilute electron gas [2,3] or of a doped excitonic insulator [4–7]. Subsequent experiments have extended the observation of ferromagnetism also to the undoped systems of CaB$_6$, SrB$_6$ and La-doped BaB$_6$ [8–10] raising new questions about the origins of the unusual magnetism.

Central to the excitonic instability model, and indeed the starting point of most thinking about the divalent hexaborides, is the presumed existence of small band overlap between the top of the boron valence states and the bottom of the cation d-conduction band at the X-point of the simple cubic Brillouin zone appropriate to these materials. Band overlap is predicted by LDA band structure calculations [11–13] and de Haas-van Alphen (dHvA) and Shubnikov-de Haas (SdH) experiments [14–16] have been interpreted in this semi-metal framework.

The well known need for many body corrections to the LDA in calculating semiconductor band gaps [17] calls into question the LDA band overlap result. Indeed a recent pseudopotential GW quasiparticle band calculation for CaB$_6$ has predicted a large 0.8 eV X-point band gap [18]. In contrast, two new all-electron GW calculations have instead predicted an intermediate 0.3 eV bandgap [19], and an unusual increased band overlap relative to LDA [20], the latter thought to be due the special character of the X-point states. The wide disparity in results for three different implementations of the GW quasiparticle band calculation scheme, which has been very successful for calculating band gaps in many common semiconductors [17], shows clearly that existing methodologies are inconsistent [21,22], applied in this case to a system with which there is no prior experience or firm experimental knowledge. Thus the question of band overlap versus a band gap (and its magnitude) is not only crucial for the novel physics of these materials but also serves as a particularly pointed test case for one of the most fundamental aspects of the modern theory of electrons in solids.

In this paper we present data on divalent hexaborides from angle resolved photoemission (ARPES) and resonant inelastic x-ray scattering (RIXS) showing a global bulk electronic structure consistent with the calculated bulk boron-block band structure, including the existence of a >1 eV X-point gap that is significantly larger than any of the three GW band calculations. For stoichiometric material there are just enough electrons to fill the boron-block bands so an X-point gap makes the material an insulator, whereas band overlap makes it a semimetal with hole and electron Fermi surfaces that enclose equal volumes. Thus the new band gap model, first suggested to the community by Ref. 18 and experimentally confirmed here, requires the reinterpretation of previous bulk sensitive experiments [14–16,23–25] and also the recognition that the presence of measured metallic carrier densities of $\approx$10$^{19}$-10$^{20}$ cm$^{-3}$ can only be
explained by off-stoichiometry. Furthermore, Fermi surfaces measured by ARPES for SrB$_6$ and EuB$_6$ locate the chemical potential in the bottom of the conduction band and identify the carriers as n-type, consistent with the sign of the Hall coefficient [24]. Additionally it is found that the chemical potential is variable from sample to sample and is also surface dependent, not surprising for a defect dominated semiconductor. The observed excess electrons imply either excess cations or boron vacancies, almost certainly the latter since it is not likely that excess metal ions can be packed into the rigid B$_6$ sublattice. While such boron vacancies may also produce the magnetic moments [26], recent detection of Fe impurities correlated to magnetism suggest an alternate origin [27], and both possibilities suggest some similarities to dilute magnetic semiconductors [28].

Single crystal samples of CaB$_6$, SrB$_6$ and EuB$_6$ were grown from an aluminum flux using powders prepared by boro-thermally reducing cation oxides [23]. ARPES experiments were performed both at the undulator beamline 10.0 of the Advanced Light Source synchrotron and at the Ames/Montana beamline of the Synchrotron Radiation Center (SRC) at the University of Wisconsin. Samples oriented by Laue diffraction were cleaved in situ to reveal a [100] surface just before the measurement, which was done at a sample temperature of 20-30 K and in a vacuum of $\approx 4 \times 10^{-11}$ Torr. A photon energy of 30 eV was used to probe the $\Gamma$-X band structure, a value internally consistent with an “inner potential step” of 11.2 eV determined for EuB$_6$ experimentally [11]. ARPES data, shown with reverse grayscale intensities, is the sum of two data sets with s- and p-polarization geometries that individually exhibit strong symmetry selection rule effects that we will present and analyze elsewhere. All boron-derived theory bands (1-6) are easily identified as labeled in Fig. 1 [30]. The valence band labeled 1 is observed to lie 1.15 eV below $E_F$ while the theory conduction band 0 is not observed. This indicates that indeed it is separated by a gap from valence band 1, and that the theory underestimates the bandgap by at least 0.35 eV.

ARPES data always show the valence band structure of Fig. 1, including the X-point gap, but often the chemical potential is located in conduction band 0 above the gap to create a small X-point electron pocket. Fig. 2(a,b) presents SRC data showing only the near $E_F$ behavior for SrB$_6$ and EuB$_6$ with band labeling as in Fig. 1. Shown in Fig. 2(c,d) are $k_x/k_y$ FS maps of the X-point electron pockets for the same surfaces as for the data of Fig. 2(a,b). The maps reveal an elliptical FS contour for EuB$_6$ and a smaller, not fully resolved, FS for SrB$_6$. As defined from peak positions marked in Fig. 2(a), the observation of the bottom of the conduction band allows a quantitative measure ($1.15 \pm 0.1$ eV) of the X-point gap for SrB$_6$, approximately 40% larger than the maximum gap found in the CaB$_6$ GW band calculations. A similar gap value is inferred for EuB$_6$ in Fig. 2(b), but with larger uncertainty due to the visible smearing of spectral weight at the top of band 1. We ascribe this smearing, which occurs also for the other EuB$_6$ boron bands (not shown), but does not occur in CaB$_6$ and SrB$_6$ to the larger number of B vacancies in EuB$_6$ implied by the larger occupation of its X-point conduction band.

SdH and dHvA experiments on EuB$_6$ [14,15] also find ellipsoidal Fermi surfaces, i.e. two frequencies with the angle dependences [15] for the two extremal orbits, but with four frequencies total indicating two ellipsoids having slightly differing sizes. The semi-metallic band overlap model identifies these two FS sheets as the electron and hole pockets while an alternate interpretation, consistent with our ARPES data, is that a single electron pocket is slightly spin-split by the large internal field of the ferromagnetically ordered Eu 4$f$ moments, aided by the very high magnetic field employed in the measurements [31]. Consistent with this interpretation, dHvA studies of CaB$_6$ and SrB$_6$ reveal only two frequencies [16] as expected for a single elliptical conduction band pocket. Of the more complex “lens” and “napkin ring” FS topologies resulting from band-overlap electron-hole mixing [11,13], only the “lens” FS has a possible dHvA correspondence [16] for CaB$_6$ and SrB$_6$, and both are precluded for EuB$_6$ by the observed SdH angular depen-
ferences.

Given the logical necessity for boron vacancies, it is then not surprising that considerable variation of the chemical potential position from sample to sample and from bulk to surface is a basic aspect of divalent hexaborides. For example, the FS dimensions found for EuB$_6$ by SdH and dHvA [14,15] are different both from one another and also from those implied by the ARPES of Fig. 2. In one ARPES experiment on EuB$_6$ an X-point electron pocket was initially not present and then appeared somewhat abruptly about four hours after cleavage, but with a size smaller than that of Fig. 2 (a,c). As expected if boron vacancies are involved, this time dependent shift of the surface chemical potential was accompanied by some redistribution and shift of the boron-block bands, but always with the same band gap value observed previously. Thus, as occurs for other semiconductors, surface defects and band bending control the surface chemical potential position. Elucidating and controlling the details of the defect states for both the bulk and the surface is an essential goal for future research on these materials.

Bulk-sensitive SXE and XAS quantitatively confirm the X-point band structure of CaB$_6$ presented in Fig. 1. Fig. 3(a) compares valence emission spectra for CaB$_6$ with at-threshold (187.85 eV) and above-threshold excitation (212 eV) as indicated by arrows in the TEY absorption spectrum (Fig. 3 inset). The above-threshold SXE shows a lineshape in very good agreement with a calculated boron p-DOS for SrB$_6$ [12]. The threshold-excited RIXS spectrum, on the other hand, has a different overall profile and multiple distinct peaks including a sharp elastic emission peak (labeled e in Fig. 3) at the threshold onset energy (187.85 eV) as the result of direct radiative decay from the CB minimum. This elastic peak provides a convenient marker for relative calibration of the emission and absorption energy scales [32]. The separation of the top of the VB emission from this absorption-threshold elastic peak is a graphic signature of the existence of a bulk semiconductor band gap.

Interpreted in the framework of RIXS, the threshold excitation into the X-point CB minimum results in a superposition of coherent momentum-conserving emission and incoherent emission of various origins [29]. As done in previous RIXS studies of semiconductors [33], we can refine the RIXS analysis to highlight the k-selective features if we approximate the incoherent emission profile by the above-threshold SXE spectrum and subtract it from the RIXS spectrum with the scaling shown in Fig. 3(a). The resulting RIXS difference spectrum is shown in Fig. 3(b) with comparison to the sharpest low binding energy peaks of the X-point CaB$_6$ ARPES spectrum plotted to align peaks 2 and 3. This alignment produces excellent agreement between ARPES and RIXS for peak 1, i.e. the VB maximum. Furthermore, the PFY absorption edge is also plotted in Fig. 3(b) and it is observed that the ARPES Fermi level occurs at the onset of the PFY threshold intensity rise. Thus for CaB$_6$, we have provided a bulk confirmation of all the features of the surface-sensitive ARPES measurements, in particular, the value of the X-point band gap (1.15 eV) and the location of the chemical potential just at the bottom of the conduction band. Soft x-ray measurements of other divalent hexaborides give similar results [34,35], and SXE and ARPES of La-doped CaB$_6$ and trivalent LaB$_6$ reveal that the gap magnitude is very sensitive to the conduction band occupation [35,36].

In summary, complementary ARPES and SXE/XAS experiments on divalent CaB$_6$ quantitatively agree to provide a clear case for the existence of a large energy scale bulk band gap. Small energy scale excitonic-insulator or hybridization gap models based on X-point band overlap are thus precluded. Widely differing band gap values from pseudopotential and all-electron GW calculations illustrate the insufficiency of current theory, and our high-quality ARPES bulk band structure of CaB$_6$ sets a clear benchmark for future work. The positioning of the bulk chemical potential in the conduction band and the resulting n-type carriers observed in nominally stoichiometric samples implicate boron vacancies. The physics of the divalent hexaborides is not that of an intrinsic semi-metal, but that of a defect semiconductor.

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Fig. 1. Comparison of the experimental and theoretical band structures of CaB₆ along Γ-X. The reverse gray scale image of ARPES intensities is the sum of two data sets with 30 eV s- and p-polarized excitation. Dashed lines are from the quasiparticle GW calculation [18] giving X-point gap between bands 0 and 1.

Fig. 2. Near-E_F valence band structure for (a) SrB₆ and (b) EuB₆ along Γ-X showing small band 0 electron pockets above the X-point gap to band 1. E_F intensity maps of the X-point at hν=30 eV for (c) SrB₆ and (d) EuB₆ showing differing electron pocket sizes.

Fig. 3. (a) CaB₆ valence x-ray emission excited at-threshold (RIXS) and above-threshold (SXE) with comparison to calculated [12] boron p-DOS (dashed). (Inset) TEY absorption spectrum indicating excitation energies. (b) k-resolved RIXS difference spectrum (RIXS-SXE) with comparison to ARPES X-point spectrum showing alignment of valence band peaks and alignment of the ARPES Fermi level to the PFY absorption threshold.

An additional weak broad dispersion at the bottom of the valence band, 11 eV at Γ, is suggestive of back-folding, perhaps consistent with 2×1 surface order revealed by low energy electron diffraction of freshly cleaved CaB₆ surfaces.

Our ARPES data are taken in zero field above T_Curie ≈ 15 K and so could not display the splitting.

Absolute photon energies were calibrated to a 194.0 eV TEY peak due to surface boron oxide.


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