6 Element Strategy Initiative to Form Core Research Center for Electron Materials

 Multi probe study using synchrotron light, neutron, and muon beams –

> Youichi Murakami, Hiroshi Kumigashira, Ryosuke Kadono, Jun-ichi Yamaura

6-1 Introduction

The national project "Elements strategy initiative to form core research centers" was launched in 2012. The objective is to develop entirely new materials based on ubiquitous elements. The research is conducted primarily at four research centers, which were established in research institutes and universities. They carry out studies on (1) magnetic materials, (2) electronic materials, (3) catalysts and batteries, and (4) structural materials. This project is connected to the research center for electronic materials of Tokyo Institute of Technology. We have put much effort into evaluating and analyzing new materials, establishing material concepts, and developing techniques for evaluating materials using synchrotron light, neutron, and muon beams. We report the year's main topics: antiperovskite-type oxide Ca₃SnO thin films, gapless magnetic excitation of LaFeAsO_{0.5}D_{0.5}, two-dimensional electride Y₂C, and interstitial hydrogen in iron disulfide.

6-2 Optimization of growth conditions for antiperovskite-type oxide Ca₃SnO thin films by using a combination of synchrotron radiation analyses

Perovskite oxides and their heterostructures are well known as valuable systems showing novel functional properties. Recently, their counterparts, namely antiperovskite oxides A_3BO have been attracting much attention as an alternative platform for searching unique physical properties. Immediately after the theoretical prediction that some of the A_3BO family have three-dimensional (3D) Dirac Fermions [1], a number of experimen-



Fig. 1: The valence band spectrum of a Ca_3SnO film, together with the density of states obtained from the first principle calculation. To emphasize the gap-like feature in the Ca_3SnO film near the Fermi level (E_F) of the sample, the Fermi edge of a gold film is superimposed.

tal and theoretical efforts has been devoted to exploring possible bulk Dirac Fermions in A_3BO [2,3]. Because this unique electronic structure appears not at the surface but in the bulk, perovskite and antiperovskite heterostructures might also be a promising field to explore novel physical properties in the light of the analogies to the perovskite oxide heterostructures. However, despite these intriguing research subjects, the study on the growth of antiperovskite films is limited, owing to its unusual anionic state and air sensitivity [2,3].

In this study, we report the epitaxial growth of antiperovskite Ca₃SnO films on (001)-oriented cubic yttria-stabilized zirconia (YSZ) substrates by using the pulsed laser deposition (PLD) technique. We have tuned the growth conditions by

monitoring the chemical, electronic, and crystal structures based on the combination of synchrotron radiation analyses, and eventually have succeeded in growing Ca₃SnO epitaxial films. The epitaxial nature of the films on YSZ substrates was proved by x-ray diffraction. The detailed analysis revealed that the Ca₃SnO films were epitaxially grown on the YSZ substrates with a cube-on-cube orientation relationship, although the existence of some impurity phases was found. The electronic structures as well as the chemical composition of the grown films were examined by x-ray photoemission spectroscopy. As shown in Fig. 1, the shape of the valence band spectra was qualitatively reproduced by the first principles calculation, although there were discrepancies between the two near the Fermi level. These results demonstrate that antiperovskite films are synthesized by using the PLD technique and the synchrotron radiation analysis is a powerful tool to optimize the growth conditions of films.

6-3 Gapless magnetic excitation in a heavily electron-doped antiferromagnetic phase of LaFeAsO_{0.5}D_{0.5}

Since the discovery of the first iron-based superconductor (FeSC), a wide variety of FeSC families have been discovered [4, 5]. The different FeSC families commonly contain a conductive FePn4 or FeCh4 (Pn = P, As; Ch = Se, Te) layer and a blocking layer, and have a similar Fe 3d electronic structure. Typically, superconductivity emerges owing to the suppression of structural (orbital ordering) and magnetic phase transitions by carrier doping into the Fe layer. Recently, a doping technique for producing a higher electron concentration for FeSC 1111 systems has been developed in which H⁻ is used instead of F⁻. Remarkably, owing to the heavy electron doping, a second antiferromagnetic phase appears in Laand Sm-1111 systems just after the disappearance of the superconducting phase [6]. Several subsequent studies have all suggested that the heavy electron doping enhances electron correlations and the localized character in the second antiferromagnetic phase. These studies suggest that spin and/or orbital fluctuations from the strongly correlated phase significantly contribute to the high Tc in 1111 compounds. Therefore, it is indispensable to understand magnetic excitations



Fig. 2: Energy dependence of the imaginary part of the dynamic magnetic susceptibility, $\chi''(Q_{AF1(2)}, E)$ at each temperature for (a) x = 0 and (b) x = 0.5. Note that the $\chi''(Q_{AF1}, E)$ with Ei = 6.4 meV could not be measured with a sufficient signal-to-noise ratio. The intensities for different E_i 's and x's were normalized by using incoherent elastic scattering intensities to facilitate the comparison. Solid lines are guides for the eyes.

in the heavily electron-doped antiferromagnetic phase.

 $LaFeAsO_{1-x}H_x$, the target material in this study, is the simplest 1111 system, because La³⁺ does not have a magnetic moment. The LaFeAsO exhibits a structural transition with decreasing temperature from P4=nmm (tetragonal) to Cmme (orthorhombic) at Ts = 155 K. On further cooling, a magnetic phase transition occurs at $T_{\rm N} = 137$ K. A magnetic structure in this phase (AF1 phase) is a collinear stripe type with a propagation vector $Q_{AF1} = (1, 0, 1/2)$ in reciprocal lattice units (orthorhombic Cmme unit cell). The magnetic moments, which have a magnitude of 0.63 $\mu_B/$ Fe, are parallel/antiparallel to the a direction. The magnetic ordering in the AF1 phase is compatible with a Fermi surface (FS) nesting scenario; it is regarded as a spin density wave (SDW) of itinerant electrons owing to FS nesting. Meanwhile, the LaFeAsO_{0.5}H_{0.5} also exhibits a magnetic phase transition at $T_N = 89$ K (AF2 phase) subsequent

to a tetragonal-orthorhombic structural transition at $T_s \sim 95$ K. The space group changes from *P*4/ *nmm* to *Aem*2 during this transition. The magnetic modulation vector, **Q**_{AF2}, is (1,0,0), and the magnetic moments (1.21 μ_B /Fe) are parallel/antiparallel to the *b* direction. According to band calculations, the nesting is weakened by the electron doping monotonically with *x*, and therefore, the magnetic ordering in the AF2 phase has little influence on FS nesting. Thus, magnetic excitations in the AF2 phase are expected to exhibit features distinct from the typical SDW magnetism in LaFeAsO and in 122 families, such as BaFe₂As₂.

In this study, we have measured magnetic excitations in the AF1 (x = 0) and AF2 (x = 0.5) phases by powder inelastic neutron scattering on LaFeAsO_{1-x}D_x samples. Unlike other parent compounds of the FeSC, the magnetic excitation gap in LaFeAsO_{0.5}D_{0.5} was not detected below the lowest measured temperature of 4 K, as shown in Fig. 2 [6]. This observation is unique in the parent compounds of FeSCs. This result can be understood as an effect of quasi-isotropy within the ab plane, which is consistent with the band calculation result that the dxy orbital plays the dominant role in the magnetism of LaFeAsO_{0.5}H_{0.5}. In addition, the intensities of the magnetic excitations in this phase are much stronger than those in non-doped LaFeAsO. Even in the paramagnetic phase, the magnetic excitation in LaFeAsO_{0.5}D_{0.5} persists [6]. These results corroborate recent studies showing that the electron doping enhances the localized nature in this system.

6-4 Local electronic structure and hydrogen site in 2D-electride Y₂C

Electrides are a class of materials in which electrons serve as anions (without atomic nuclei) in the positively charged lattice framework sustained by covalent bonds. These materials have drawn much attention because of their promising properties such as high electrical conductivity, low work function, and significant catalytic activity in their ideal form. Recently, Ca₂N, a layered nitride compound, was reported to be an electride [8,9], where electrons were presumed to be extended in two dimensions (2D) over the interlamellar space between the calcium layers [10]. This triggered a theoretical search for candidate compounds as 2D-electrides, where yttrium carbide Y₂C was in-



Fig. 3: Crystal structure of Y_2C . Blue and gray spheres represent Y and C atoms, respectively, and the region hatched in orange shows the 2D-electron layer.

cluded in several of them [11].

The very recent success in the actual synthesis of Y₂C has put the compound under the spot light, as it crystalized into a lattice structure common to Ca₂N [11,12]. As shown in Fig. 3, Y₂C belongs to the space group $R\overline{3}m$ with a lattice constant for the a(c) axis being 3.6164 (17.9651) Å. A DFT calculation suggests 2D electride features for this compound are similar to Ca₂N [12], where the electron band near the Fermi energy consists of Y 4d orbitals, and 2D electronic states (s orbital character) are present between the Y layers. While the predicted band structures [9,12] have been confirmed by ARPES [10,13], the interesting possibility of ferromagnetic instability associated with electride bands suggested for Y₂C [14] has been yet to be examined experimentally. To this end, implanted muon spin rotation/relaxation (µSR) is the only practical technique, considering the low sensitivity of $^{89}\text{Y-NMR}$ (~1/20 of $\mu\text{SR})$ and the negligible abundance of ¹³C.

Meanwhile, the compound has been also found to be a hydrogen storage material, where the site and local electronic properties of interstitial H atoms remain to be an important issue. In particular, the information in their dilute limit would be crucial in view of the possible applications of Y_2C as a matrix of catalysts for H-related chemical



Fig. 4: (a) Temperature dependence of the magnetic susceptibility $\chi = M/H$ (left axis) and muon Knight shift K_{μ} (right axis) for the polycrystalline sample measured under $B_{\text{ext}} = 6$ T. (b) Clogston-Jaccarino (K_{μ} - χ) plot for the polycrystalline sample. The dashed line represents the best fit obtained by the linear function and its gradient corresponds to the hyperfine-coupling constant A_{μ} .

reactions, for which an implanted muon can serve as a unique tool because it behaves as a pseudohydrogen in matter. Hereafter, we will call this particle "muogen" (Mu) in the context of a muon as a hydrogen isotope.

In FY2018, we reported a μ SR study on the magnetic properties of Y₂C for polycrystalline (pc) [12] and single-crystalline (sc) samples [15], which showed different behaviors in their bulk magnetic property; i.e., the former exhibited Curie–Weiss behavior whereas the latter was Pauli paramagnetic in the uniform susceptibility (χ) [16]. This phenomenon would be of crucial importance for assessing the predicted instability to the Stoner ferromagnetism.

From μ SR measurements under zero external field (ZF- μ SR), it was inferred that both samples showed no sign of magnetic order (including



Fig. 5: Schematic illustration of the Y_4 site, which is at the center of the Y tetrahedron next to the Y_6 site.

antiferromagnetism) at low temperatures below 0.024 K. Moreover, muon Knight shift measurements clearly indicated that the observed Curie– Weiss behavior of pc samples (see Fig. 4 (a)) was not due to impurities, but caused by localized moments at the Y sites (1~2 μ_B , with μ_B being the Bohr magneton) as evidenced by the fact that the observed shift was proportional to χ (see Fig. 4 (b)). Here, the shift K_{μ} is related to the local (microscopic) susceptibility χ_{loc} via the equation

$K_{\mu} = A_{\mu \chi_{\rm loc}} / N_{\rm A} \mu_{\rm B} + K_0,$

where $A\mu$ is the muon-electron hyperfine parameter, N_A is the Avogadro number, and K_0 is the Fermi contact term. The observed relationship between K_{μ} and χ demonstrates that $\chi = \chi_{loc}$, so that χ should represent the intrinsic property of Y₂C. As discussed below, the Y moment size of ~1.1µ_B deduced from the magnitude of A_{μ} for the muon at the Y₄ site is in excellent agreement with the result of DFT calculation predicting the Y valence of 1.9+ (4d^{1.1}) from the 4d partial density of states, also corroborating with the magnitude of the Curie term (~0.605µ_B) estimated from χ .

This result points to the important role of on-



Fig. 6: Temperature dependence of molar magnetic susceptibility $\chi = M/H$ measured under 1 T (left axis) and muon Knight shift K_{μ} under $B_{\text{ext}} = 6$ T (right axis) for single-crystalline Y₂C. The external magnetic field was parallel to the c axis.

site electronic correlations (U) in understanding the electride band (as the theory predicts that the Stoner instability is suppressed by U [14]) and that a slight modulation of the local electronic state or a Fermi-level shift owing to the presence of carbon defects (often inherent) and/or impurities causes local moments at the Y sites to appear.

Regarding the muon site, it was initially inferred to be at the center of an octahedron with six Y atoms at the corners (Y₆ site) where the Hartree potential obtained by the DFT calculation (using the VASP package) exhibited a minimum. The Y₆ site was similar to that of H suggested by neutron diffraction of deuterated $Y_2C:D_x$ [17]. However, the Y moment size of 1.94(1)µ_B estimated by A_{μ} for this site resulted considerably larger than that suggested from the Curie term [16], which entailed ambiguity in the interpretation. Following the suggestion of the neutron result that the Y₄ site (the center of the Y tetrahedron next to the Y_6 site, see Fig. 5) was preferred for H at the lower density, we recently re-examined the Y moment size, assuming the Y₄ site for muons, and obtained the value $1.11(1) \mu_{B.}$ This result was far more consistent with other implications and indicates that muon (and hence H) does prefer the Y₄ site in the dilute limit.

Because the Hartree potential does not consider the local energy gain owing to the covalency associated with the orbital electron of Mu/H, the preference of Y_4 to Y_6 site strongly suggests that Mu/H forms chemical bonding to Y. This is also in line with the fact that Y can form hydrides, and suggests that H in Y_2C is not chemically active at the dilute concentration.

By contrast, the sc sample exhibited a temperature-independent negative Knight shift; i.e., a shift with opposite sign and magnitude much greater than that expected from Pauli paramagnetism (see Fig. 6) [16]. It should be noted that K_{μ} for conventional metals exhibit a positive shift, which is proportional to the density of states at the Fermi surface. The shift owing to the s electron is given by $K_{\rm s} = (8\pi/3) |\varphi_{kF}(0)|^2 \chi_{\rm p} > 0$,

where χ_p is the Pauli paramagnetic susceptibility and φ_{kF} (0) is the amplitude of the s-electron wave function at the muon position. Considering the observation that a negative Knight shift in metals with positive bulk susceptibility is limited to metals such as Ni, Pd, Pt, and those exhibiting strong s-d hybridization [18], the observed result for the sc sample may be related to the hybridization of the 4d and the electride bands. Another possibility would be the presence of orbital diamagnetism specific to the 2D electride band, the microscopic details of which are yet to be clarified. In any case, more work is needed to achieve a clearer understanding of the anomalous negative Knight shift in diamagnetic Y₂C.

6-5 Interstitial hydrogen in iron disulfide: a muon study

Iron disulfide (FeS₂), also known as the mineral pyrite or fool's gold, has significant scientific interest and technological applications. It was first explored as a photovoltaic semiconductor in the mid-1980s [19] and has attracted renewed attention in recent years [20-22] as other thin-film absorber materials like amorphous silicon, CdTe, and Cu(In,Ga)Se (CIGS) have gained commercial success [23,24]. It is a promising optoelectronic material owing to its suitable indirect band gap (E_{g} \simeq 0.95 eV) and high absorption coefficient (>10⁵ cm⁻¹ at $E_q \pm 0.1$ eV), which opens up great potential for emerging renewable energy applications, including photovoltaics, photodetectors, and photoelectrochemical cells [21,25]. Interest in pyrite has also revived owing to its low toxicity, virtually infinite elemental abundance, and low raw material cost [20-22,26].

The main obstacle to the development of pyrite as an optoelectronic material is its low opencircuit photovoltage V_{oc} , which is typically only ~0.2 V. Traditionally, this has been attributed to surface



Fig. 7: Atomic configuration of FeS_2 and possible candidate sites for two Mu states, where isosurfaces of the Hartree potential (0.3 eV above the -11.387 eV potential minimum) are displayed by blue hatched areas.

defect states in FeS₂, its heterogeneous band gap, and Fermi level pinning [27]. However, recent theoretical investigations suggest many different views, including one that proposes that sulfur vacancies are not the cause of these difficulties [27]. Meanwhile, it has been known for decades that natural pyrite crystals often exhibit n-type conductivity of unknown origin with activation energies less than 0.01 eV [28]. There is circumstantial evidence that hydrogen is involved in this process [19]. Moreover, electrochemical experiments suggest strikingly fast hydrogen diffusion in pyrite (corresponding diffusion coefficient $D_{\rm H}$ ~ 2 × 10⁻⁶ cm²/s, comparable to that in bcc metals at ambient condition) [29,30], which is further enhanced after the saturation of defects by hydrogen [30]. Considering that hydrogen is the most ubiquitous impurity, one may be naturally led to suspect interstitial hydrogen as the cause of these mysterious electrical activities in FeS₂.

It is well established that muon can be regarded as a light proton isotope in the sense that the local structure of a muon-electron system is virtually equivalent with that of hydrogen, except for a small correction ($\simeq 0.4\%$) owing to the difference in the reduced electron mass. While the light mass of a muon ($\simeq m_p/9$, with m_p being the proton mass) often leads to the isotope effect, which is particularly distinctive in diffusion at low temperatures where the quantum tunneling process becomes dominant, a muon also simulates hydrogen diffusion via classical over-barrier jump at high temperatures.

We studied single-crystalline samples of natural pyrite (unknown origin) sliced into slabs with a plane normal to the [100] crystal axis for µSR measurements [31]. The crystal structure of FeS₂ belongs to the space group $Pa\overline{3}$ (No. 205), consisting of FeS₆ octahedrons with S vertices forming dimers between them. The powder XRD spectra indicated that the sample was in a single phase with less than 1% impurities and defects. χ was almost completely independent of temperature, except for a slight enhancement below ~20 K. A curve fit by the Curie–Weiss law for data below 50 K yielded an effective moment of 0.0125(3) μ_B , which corresponds to an atomic concentration of 1.11(3) \times 10²⁰ cm⁻³ for spin S = 1 paramagnetic impurities (e.g., those associated with Fe vacancies, V_{Fe} [26]). This paramagnetic defect center was labeled X_{p} . The negative sign of the Hall coefficient $R_{\rm H}$ indicated that the residual carriers were dominated by n-type impurities. The temperature dependence of $R_{\rm H}$, as well as that of electrical resistivity ρ_{xx} , suggested that there were at least two species of unidentified donor centers with different activation energies whose origins are hereby labeled X_i (i = 1, 2). They accompany donor levels E_{Xi} with $|E_{X1}|/k_{\rm B} \simeq 102$ K and $|E_{X2}|/k_{\rm B}$ $k_{\rm B} \gg 200$ K, yielding electronically active carriers of $n_{\rm e} = 1-2 \times 10^{17} \, {\rm cm}^{-3}$ ($\simeq 4-8$ atomic ppm). These figures indicated the relatively good quality of the sample in terms of electrically active purities.

Our implanted-muon study indicated that there were four electronically inequivalent Mu states in FeS₂, i.e., two paramagnetic centers labeled Mu_p and Mu_p^{*} and two diamagnetic centers labeled Mu_d and Mu_d^{*}. The magnitude of the hyperfine parameter [$\omega_{hf}/2\pi \simeq 411(40)$ MHz for Mu_p and $\omega_{hf} = 0$ for Mu_d], combined with the Hartree potential calculation, suggested that Mup occupies an Fe-tetrahedron center corresponding to the S-S antibonding site (see Fig. 7). It was inferred from time-dependent muon polarization that Mup underwent fast conversion to a diamagnetic state Mu_{d^*} ($\omega_{hf} = 0$, exhibiting depolarization due to spin/ charge exchange interaction), which suggests the possibility of diffusion-limited trapping of Mup by defects/impurities to form complex states. Mud was tentatively attributed to an effective-mass-like shallow donor/acceptor state or a sulfhydryl-like SMu⁻ complex that served as the donor by releasing an electron upon formation via the following process: $S_2^{2^-}$ + Mu \rightarrow S²⁻ + SMu⁻ + e⁻. The small ionization energy ($E_{\rm p} \simeq 10$ meV for Mu_p and $E_{\rm d} \leq$ 1 meV for Mu_d) indicated that the electronic levels associated with these Mu centers were situated near (or merged to) the band edge. Meanwhile, the electronic state of Mup* inferred from a positive frequency shift under a high transverse field was interpreted as Mup undergoing strong dynamical modulation of ω_{hf} , probably owing to fast diffusion. These observations suggested that interstitial hydrogen would also serve as an electronically active impurity in FeS₂.

References

- T. Kariyado, and M. Ogata, J. Phys. Soc. Jpn. 80, 083704 (2011).
- [2] Y. F. Lee et al., Appl. Phys. Lett. **103**, 112101 (2013).
- [3] D. Samal et al., APL Mater. 4, 076101 (2016).
- [4] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc **130**, 3296 (2008).
- [5] H. Hosono and K. Kuroki, Physica C 514, 399 (2015).
- [6] M. Hiraishi, S. Iimura, K. M. Kojima, J. Yamaura, H. Hiraka, K. Ikeda, P. Miao, Y. Ishikawa, S. Torii, M. Miyazaki, I. Yamauchi, A. Koda, K. Ishii, M. Yoshida, J. Mizuki, R. Kadono, R. Kumai, T. Kamiyama, T. Otomo, Y. Murakami, S. Matsuishi, and H. Hosono, Nat. Phys. **10**, 300 (2014).
- [7] Hiromu Tamatsukuri, Haruhiro Hiraka, Kazuhiko Ikeuchi, Soshi limura, Yoshinori Muraba, Mitsutaka Nakamura, Hajime Sagayama, Jun-ichi Yamaura, Youichi Murakami, Yoshio Kuramoto, and Hideo Hosono, Phys. Rev. B 98, 174415 (2018).
- [8] C. M. Fang, G. A. de Wijs, R. A. de Groot, H.
 T. Hintzen, and G. de With, Chem. Mater. 12, 1847 (2000).
- [9] K. Lee, S. W. Kim, Y. Toda, S. Matsuishi, and H. Hosono, Nature (London) **494**, 336 (2013).
- [10] J. S. Oh, C.-J. Kang, Y. J. Kim, S. Sinn, M. Han, Y. J. Chang, B.-G. Park, S. W. Kim, B. I. Min, H.-D. Kim, and T. W. Noh, J. Am. Chem. Soc. **138**, 2496 (2016).

- [11] T. Inoshita, S. Jeong, N. Hamada, and H. Hosono, Phys. Rev. X 4, 031023 (2014).
- [12] X. Zhang, Z. Xiao, H. Lei, Y. Toda, S. Matsuishi, T. Kamiya, S. Ueda, and H. Hosono, Chem. Mater. 26, 6638 (2014).
- [13] K. Horiba, R. Yukawa, T. Mitsuhashi, M. Kitamura, T. Inoshita, N. Hamada, S. Otani, N. Ohashi, S. Maki, J. Yamaura, H. Hosono, Y. Murakami, and H. Kumigashira, Phys. Rev. B 96, 045101 (2017).
- [14] T. Inoshita, N. Hamada, and H. Hosono, Phys. Rev. B 92, 201109(R) (2015).
- [15] S. Otani, K. Hirata, Y. Adachi, and N. Ohashi, J. Cryst. Growth **454**, 15 (2016).
- [16] M. Hiraishi, K. M. Kojima, I. Yamauchi, H. Okabe, S. Takeshita, A. Koda, R. Kadono, X. Zhang, S. Matsuishi, H. Hosono, K. Hirata, S. Otani, and N. Ohashi, Phys. Rev. B 98, 041104(R) (2018).
- [17] J. P. Maehlen, V. A. Yartys, and B. C. Hauback, J. Alloys Compd. **351**, 151 (2003).
- [18] F. N. Gygax, A. Hintermann, W. Ru⁻egg, A. Schenck, W. Studer, A. J. van der Wal, and L. Schlapbach, Hyperfine Interact. **17**, 377 (1984).
- [19] A. Ennaoui, S. Fiechter, Ch. Pettenkofer, N. Alonso-Vante, K. Bu⁻ker, M. Bronold, Ch. Ho⁻pfner, and H. Tributsch, Sol. Energy Mater. Sol. Cells **29**, 289 (1993).
- [20] C. Wadia, Y. Wu, S. Gul, S. K. Volkman, J. Guo, and A. P. Alivisatos, Chem. Mater. 21, 2568 (2009).
- [21] J. Puthussery, S. Seefeld, N. Berry, M. Gibbs, and M. Law, J. Am. Chem. Soc. 133, 716 (2011).
- [22] Y. N. Zhang, J. Hu, M. Law, and R. Q. Wu, Phys. Rev. B 85, 085314 (2012).
- [23] A. Bosio, A. Romeo, D. Menossi, S. Mazzamuto, and N. Romeo, Crystal Res. Technol. 46, 857 (2011).
- [24] M. Green, J. Mater. Sci.: Mater. Electron. 18, 15 (2007).
- [25] D.-Y. Wang, Y.-T. Jiang, C.-C. Lin, S.-S. Li, Y.-T. Wang, C.-C. Chen, and C.-W. Chen, Adv. Mater. 24, 3415 (2012).
- [26] C. Wadia, A. P. Alivisatos, and D. M. Kammene, Environ. Sci. Technol. 43, 2072 (2009).
- [27] L. Yu, S. Lany, R. Kykyneshi, V. Jieratum, R. Ravichandran, B. Pelatt, E. Altschul, H. A. S. Platt, J. F. Wager, D. A. Keszler, and A.

Zunger, Adv. Energy Mater. 1, 748 (2011).

- [28] R. Schieck, A. Hartmann, S. Fiechter, R. Ko[°]nenkamp, and H. Wetzel, J. Mater. Res. 5, 1567 (1990).
- [29] S. Wilhelm, J. Vera, and N. Hackerman, J. Electrochem. Soc. **130**, 2129 (1983).
- [30] M. Bungs and H. Tributsch, Ber. Bunsengesellschaft Phys. Chem. **101**, 1844 (1997).
- [31] H. Okabe, M. Hiraishi, S. Takeshita, A. Koda,
 K. M. Kojima, and R. Kadono, Phys. Rev. B
 98, 075210 (2018).