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# Characterization of vacancy defects in Cu(In,Ga)Se<sub>2</sub> by positron annihilation spectroscopy

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## Characterization of vacancy defects in Cu(In,Ga)Se<sub>2</sub> by positron annihilation spectroscopy

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The photovoltaic performance of Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> (CIGS) materials is commonly assumed to be degraded by the presence of vacancy-related defects. However, experimental identification of specific vacancy defects remains challenging. In this work we report positron lifetime measurements on CIGS crystals with  $x = 0$ , and  $x = 0.05$ , saturation trapping to two dominant vacancy defect types, in both types of crystal, is observed and found to be independent of temperature between 15–300 K. Atomic superposition method calculations of the positron lifetimes for a range of vacancy defects in CIS and CGS are reported. The calculated lifetimes support the assignment of the first experimental lifetime component to monovacancy or divacancy defects, and the second to trivacancies, or possibly the large In-Se divacancy. Further, the calculated positron parameters obtained here provide evidence that positron annihilation spectroscopy has the capability to identify specific vacancy-related defects in the Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> chalcogenides. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4972251>]

### I. INTRODUCTION

The efficiency of thin film Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> (CIGS) chalcogenide solar cells continues to improve,<sup>1,2</sup> with recent gains resulting from the developments in alkali post deposition treatments.<sup>2,3</sup> The deposited CIGS layer is commonly  $p$ -doped by lattice defects.<sup>2</sup> The alkali elements introduced by the post deposition treatments dope the film and modify the interfaces,<sup>3</sup> and may passivate the lattice defects.<sup>2</sup> Device performance of CIGS solar cells can also be affected by the presence of metastable defects in the absorbing layer.<sup>4–8</sup> Further gains in efficiency are being hampered by the increased importance of defect mediated recombination with increasing Ga content toward the optimal value.<sup>9</sup> Further, it has been found that by varying the Se flux used for CIGS thin film growth cell efficiency is suppressed for low values, and that this correlates with an increase in vacancy-related defects.<sup>10</sup> The evidence for the importance of lattice defects, and the potential to gain further improvements in device performance, has motivated detailed density functional theory (DFT) studies on point defects in Cu(In,Ga)Se<sub>2</sub> materials.<sup>11–17</sup> The aim is to understand the nature and the possible influence on material performance of specific defects. It has been proposed that the device metastabilities result from the presence of DX-type centers, and these include an In (or Ga) on Cu antisite defect with one (In<sub>Cu</sub>-V<sub>Cu</sub>) or two nearest neighbor Cu vacancies (In<sub>Cu</sub>-2V<sub>Cu</sub>).<sup>12,18</sup> The commonly observed as-grown sample  $p$ -type conductivity has been attributed to the Cu-vacancy,<sup>7</sup> while the V<sub>Se</sub>V<sub>Cu</sub> divacancy has been considered as plausible candidate for the important donor defect 0.8 eV above the valence band, and some of the metastability in CIGS.<sup>7</sup> However, the recent hybrid functional DFT calculations,

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TABLE I. Calculated positron lifetime values (ps) for vacancy-related defects in CuInSe<sub>2</sub>. Note Ref. 22 also gives values scaled to obtain agreement with the experimentally inferred bulk lifetime.

	Ref. 22	Ref. 22 (Scaled)	Ref. 21	Ref. 23	Ref. 20	This work
Bulk	228	235	240	262	232	
$V_{\text{Cu}}$	243	250	262		271	267
$V_{\text{Cu}}^{-1}$						260
$V_{\text{In}}$	249	257	284			302
$V_{\text{In}}^{-3}$						269
$V_{\text{Se}}$	245	253	257	289		279
$V_{\text{Se}}^0$						295
$V_{\text{Se}}^{-2}$						285
$V_{\text{Cu}} V_{\text{In}}$	264	272	291			309
$V_{\text{Cu}} V_{\text{Se}}$	292	301	316		307	343
$V_{\text{In}} V_{\text{Se}}$	298	307	328			369
$2V_{\text{Cu}}$			277			287
$2V_{\text{Se}}$			278			304
$2V_{\text{In}}$			298			323
$\text{In}_{\text{Cu}} 2V_{\text{Cu}}$						272
$V_{\text{Se}} 2V_{\text{Cu}}$			344		331	380
$V_{\text{Cu}} V_{\text{In}} V_{\text{Se}}$	326	336	359			403

which reproduce the experimental bandgap more accurately and so can estimate the positions of defect energy levels, provide evidence against some of the above assignments.<sup>14,16</sup>

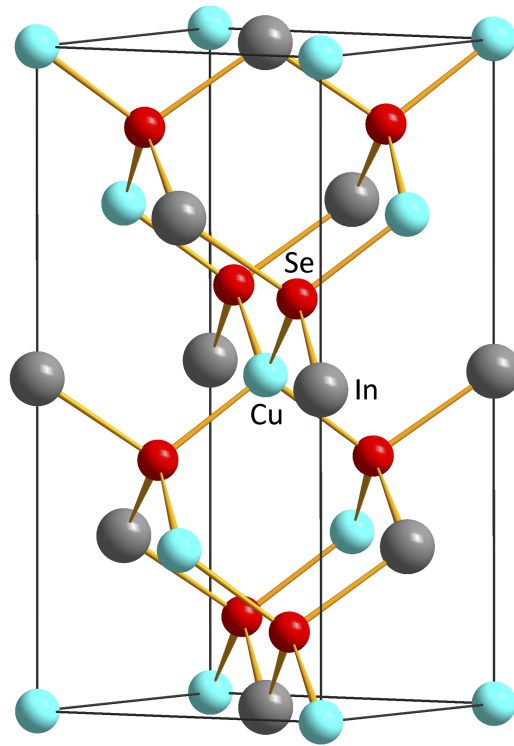
Experimental detection and identification of vacancy-related defects in CIGS materials remains challenging. Positron annihilation spectroscopy (PAS) techniques, have specific sensitivity to vacancy defects in neutral or negative charge states and can detect concentrations less than  $10^{16} \text{ cm}^{-3}$ .<sup>19</sup> The lifetime of the localized positron state is sensitive to the size of the open volume, and the chemical nature of the near neighbor atoms dominate the high electron momentum distribution sampled by the positron.<sup>19</sup> These quantities can be measured using positron annihilation lifetime spectroscopy (PALS), and coincidence Doppler broadening spectroscopy (CDBS), respectively. Previously reported DFT calculations of positron lifetime values for vacancy defects in CuInSe<sub>2</sub> are given in Table I.<sup>20–23</sup> A broadly similar trend in lifetime values with vacancy defect type is observed. Positron lifetime measurements on CuInSe<sub>2</sub> crystals have provided evidence for the perfect lattice, bulk, positron lifetime of approximately 235–240 ps.<sup>22,24</sup> It has not, however, been possible to clearly establish the vacancy defect lifetimes, a range of values have been reported.<sup>20–23,25–31</sup>

In this study we perform variable temperature positron lifetime measurements on single crystals of CuInSe<sub>2</sub> and Cu(In<sub>0.95</sub>Ga<sub>0.05</sub>)Se<sub>2</sub>. In addition, atomic superposition method DFT calculated positron lifetimes are reported for vacancy related defects in CuInSe<sub>2</sub> and CuGaSe<sub>2</sub>. These include calculations performed using available relaxed local geometries for the stable charge states of the monovacancy defects in CuInSe<sub>2</sub>.<sup>13</sup> In consequence, the two experimental positron lifetimes, observed in both crystals, are assigned. The first to monovacancy or divacancy defects, and the second to trivacancy or possibly the large divacancy defect  $V_{\text{In}} V_{\text{Se}}$ . The positron momentum distributions, also obtained from the calculations, are found to provide the possibility of further differentiation of vacancy defect local environment.

## II. METHODS

### A. Experimental details

Positron lifetime measurements were performed on crystal samples of CuInSe<sub>2</sub> and Cu(In<sub>0.95</sub>Ga<sub>0.05</sub>)Se<sub>2</sub>. For each composition two adjacent  $\sim 8 \times 8 \times 1 \text{ mm}^3$  samples were cut from a single crystalline ingot grown using the vertical Bridgman technique.<sup>32</sup> Measurements were performed with direct deposit positron sources on CIS, and with positron sources supported on  $8 \mu\text{m}$

FIG. 1. Schematic of the ideal CuInSe<sub>2</sub> lattice.

Kapton on CIGS, using conventional fast-fast coincidence spectrometers,<sup>33</sup> the instrument timing resolution functions (IRF) were obtained from measurements on directly deposited aluminum before and after the sample measurements. Room temperature spectra contained greater than  $5 \times 10^6$  counts and were performed using a spectrometer with a 203 ps full width half maximum (FWHM) IRF. Variable temperature measurements using a system with a 265 ps FWHM IRF. Corrections for source annihilation events were performed assuming the known lifetime for Kapton foil,<sup>34</sup> and using the procedures outlined elsewhere.<sup>33</sup>

### B. Computational details

The calculations were performed with the MIKA/Doppler package, where the electron density of the solid is approximated by the non-self-consistent superposition of free atom electron densities in the absence of the positron (the so-called ‘conventional scheme’). This approximation to the complete two-component density functional theory (TCDFT) has been found to give positron lifetimes close to TCDFT as well as experimental values.<sup>19,35,36</sup> The electron-positron enhancement factor obtained from the data of Arponen and Pajanne,<sup>37</sup> both the original by parameterization by Boroński and Nieminen (BN),<sup>38</sup> described within the local density approximation (LDA), and with an expression obtained by Barbiellini and co-workers,<sup>39,40</sup> (referred to as AP) described within the generalized gradient approximation (GGA) were used. The calculations were performed with  $I\bar{4}2d$  structure (Fig. 1) using  $4 \times 4 \times 4$ , 1024 atom, supercells of CuInSe<sub>2</sub>,<sup>41</sup> and CuGaSe<sub>2</sub>.<sup>42</sup> Calculations for the specific charge states of the monovacancy defects relaxed the vacancy nearest neighbor atomic positions as described by Oikkonen *et al.*<sup>13</sup> A value of 10 was assumed for the CuInSe<sub>2</sub> high frequency dielectric constant.

## III. RESULTS AND DISCUSSION

The room temperature positron lifetime spectra from both CuInSe<sub>2</sub> and Cu(In<sub>0.95</sub>Ga<sub>0.05</sub>)Se<sub>2</sub> were best fitted to two lifetime components, these are given in Table II.<sup>36</sup> The first lifetime value is

TABLE II. Room temperature positron lifetime results for CuInSe<sub>2</sub> and Cu(In<sub>0.95</sub>Ga<sub>0.05</sub>)Se<sub>2</sub> crystal samples.

	$\tau_1$ (ps)	$I_1$ (%)	$\tau_2$ (ps)	$\tau_m$ (ps)
CuInSe <sub>2</sub>	269(3)	82(6)	360(15)	283(3)
Cu(In <sub>0.95</sub> Ga <sub>0.05</sub> )Se <sub>2</sub>	267(4)	86(3)	371(10)	280(4)

greater than the accepted bulk lifetime,  $\sim 235$ – $240$  ps,<sup>22,24</sup> demonstrating that saturation trapping to vacancy related defects occurs in both types of crystal samples. Measurements were performed down to 15 K, and the mean positron lifetime was found to be constant through the temperature range for both CuInSe<sub>2</sub> and Cu(In<sub>0.95</sub>Ga<sub>0.05</sub>)Se<sub>2</sub>. Both samples exhibited dominate trapping to a component with a lifetime of approximately 268 ps and an intensity in the range 82 % to 86 %, the second lifetime value was approximately 365 ps (Table II). The absence of any temperature dependence for the mean lifetime is in contrast to previous measurements on electron irradiated CuInSe<sub>2</sub> crystals where a reduction in mean lifetime toward the bulk value was observed, consistent with the presence of negatively charged, weak binding energy, positron trapping centers, for example acceptor impurities without open volume.<sup>22</sup> The temperature independence of the mean lifetime observed here provides evidence that the ratio of the defect specific trapping coefficients for the dominant vacancy-related defects responsible for the  $\sim 268$  ps and  $\sim 365$  ps lifetime components are independent of temperature, and is consistent with both defects having the same charge state, either neutral or negative.<sup>43</sup>

Previous positron lifetime studies of Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> materials have normally reported only the mean lifetime.<sup>21,22,25</sup> Recently, a careful variable energy Doppler broadening spectroscopy (VE-DBS) study of series Cu(In<sub>0.55</sub>Ga<sub>0.45</sub>)Se<sub>2</sub> and CuGaSe<sub>2</sub> coevaporated films, grown with varying beam equivalent pressures, has been made and included VE-PALS measurements on the CIGS films.<sup>20</sup> The positron lifetime measurements showed saturation trapping was occurring in all the films and two lifetime components were resolved. The first varied in the approximate range 250–330 ps, dependent on film and implantation energy, the second component lifetime value was in the range  $\sim 440$  –  $500$  ps and had an intensity that varied from approximately 5 % to 70 %. The first lifetime value was attributed to monovacancy or small vacancy clusters, for example divacancy defects, the second lifetime component was clearly identified as due large vacancy clusters.<sup>20</sup> The values of the dominant first lifetime component reported here for crystal samples of CIGS and CIS (Table II) are within the range reported by Uedono *et al.*<sup>20</sup>

To provide insight on the nature of the vacancy-related defects responsible for the two lifetimes observed (Table II), it is necessary to compare these to theoretical lifetime values calculated by DFT. The results obtained here, and in previous calculations, for vacancy defects are given in Table I for CuInSe<sub>2</sub> and in Table III for CuGaSe<sub>2</sub>.

Polity *et al.*,<sup>22</sup> used superposition of free atom electron densities method, but with the LDA and the BN enhancement factor. The resulting defect lifetimes were assumed to be too low, based on a comparison of the calculated bulk lifetime with the experimental inferred value, in consequence the calculated lifetimes were increased by 3 % (Table I). Similar atomic superposition calculations using

TABLE III. Positron lifetime values (ps) calculated by atomic superposition DFT, using AP enhancement factor, for vacancy-related defects in CuGaSe<sub>2</sub>.

	This work	Ref. 20
$V_{\text{Cu}}$	258	257
$V_{\text{Ga}}$	266	
$V_{\text{Se}}$	268	
$V_{\text{Cu}} V_{\text{Ga}}$	281	
$V_{\text{Cu}} V_{\text{Se}}$	332	303
$V_{\text{Ga}} V_{\text{Se}}$	340	
$V_{\text{Se}} 2V_{\text{Cu}}$	370	326
$V_{\text{Cu}} V_{\text{Ga}} V_{\text{Se}}$	379	

LDA and BN performed here give a bulk lifetime value of 228 ps, in agreement with the previous report.<sup>22</sup> Ishibashi and co-workers,<sup>21</sup> reported an extensive set of calculated lifetimes (Table I), obtained using LDA-BN.<sup>44</sup> Recently, positron lifetime values calculated by the projector augmented-wave (PAW) method with the GGA for selected defects in CIS and CGS have been reported,<sup>20</sup> see Tables I and III.

Tables I and III include comparison of vacancy defect positron lifetime values obtained here using atomic superposition with GGA and AP enhancement with the PAW-GGA values from Uedono *et al.*<sup>20</sup> There is close agreement for the Cu monovacancy, for both CIS and CGS. The lifetime values increase with increasing vacancy cluster size, but the divacancy and trivacancy lifetimes obtained by PAW-GGA are smaller (Tables I and III). The dominant experimental first lifetime values of 269(3) ps for CuInSe<sub>2</sub> and 267(4) ps for Cu(In<sub>0.95</sub>Ga<sub>0.05</sub>)Se<sub>2</sub> (Table II) are consistent with monovacancy defects or with divacancies, for example  $2V_{\text{Cu}}$ ,  $2V_{\text{Se}}$ ,  $\text{In}_{\text{Cu}}2V_{\text{Cu}}$  or  $V_{\text{Cu}}V_{\text{In}}$ . The experimentally observed second lifetime component, 360(15) ps for CuInSe<sub>2</sub> and 371(10) ps for Cu(In<sub>0.95</sub>Ga<sub>0.05</sub>)Se<sub>2</sub> (Table II) is consistent with trivacancy defects such as  $V_{\text{Se}}2V_{\text{Cu}}$  or  $V_{\text{Cu}}V_{\text{In}}V_{\text{Se}}$ , or possibly the larger divacancy defect,  $V_{\text{In}}V_{\text{Se}}$ .

Despite the simplicity of the atomic superposition calculations they have demonstrated satisfactory agreement with experimental lifetime values, for example in perovskite oxide materials and for CdTe.<sup>45–47</sup> The calculations are efficient and rapid, they also enable lifetime values to be obtained using local atomic positions derived from sophisticated first principles calculations. Table I compares the lifetime values obtained from unrelaxed monovacancies in CIGS with those for the relaxed local environments of stable charge state configurations obtained from hybrid function calculations.<sup>13</sup> These charge state dependent local relaxations can have a marked effect, for example the calculated Se vacancy lifetime, reduces by approximately 30 ps for the  $-3$  charge state (Table I).

The calculated positron lifetimes shown in Tables I and III suggest a fundamental limitation on the capability of positron lifetime measurements to identify specific vacancy-related defects in these chalcogenide semiconductors; a number of defects have lifetimes that are too similar to be experimentally resolved. It is of interest to investigate the capability of coincidence Doppler broadening spectroscopy (CDBS).<sup>19</sup> The method sensitively detects positron annihilation events with high momentum core electrons, these have low probability but for positrons localized at vacancy defects they provide chemical information on the nature of the near neighbor atoms. Spectra are typical a ratio against a perfect lattice momentum spectrum, measured using a low defect density sample. These ratio spectra most clearly demonstrate the spectral feature characteristic of the local environment

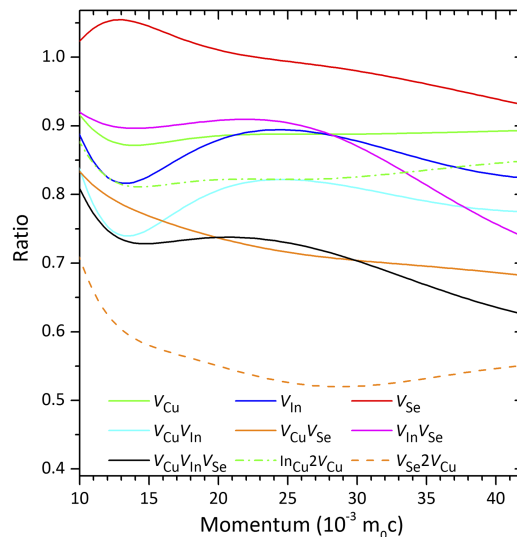


FIG. 2. Atomic superposition calculated coincidence Doppler spectroscopy ratio spectra for various vacancy-related defects in CuInSe<sub>2</sub> using unrelaxed local structures. The momentum distribution is shown as a ratio against that calculated for defect free CuInSe<sub>2</sub>.

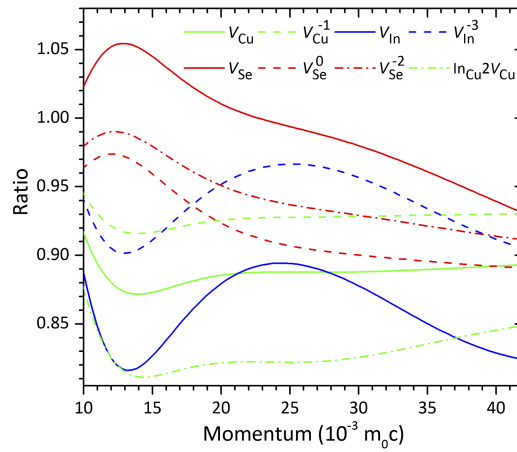


FIG. 3. Atomic superposition DFT calculated coincidence Doppler spectroscopy ratio spectra for various relaxed states of the monovacancy defects in CuInSe<sub>2</sub>. The spectra obtained using unrelaxed geometries for the defects; In<sub>Cu</sub>2V<sub>Cu</sub> is included for comparison.

of specific defects. Atomic superposition calculations have been shown to yield CDB spectra that are in agreement with experiment.<sup>48–50</sup> The method provides an adequate description of the high, core electron, momentum region which contains well-defined features characteristic of individual elements.<sup>51,52</sup>

The calculated CDBS ratio spectra for the unrelaxed vacancy defects in CuInSe<sub>2</sub> are shown in Fig. 2, and are extended to include the relaxed local structures for the monovacancy defects in Fig. 3. Only the high momentum regions greater than  $10 \times 10^{-3} m_0c$ , for which annihilation with core electrons dominate and which can be well described by the atomic superposition method, are shown.<sup>53,54</sup> Clear features characteristic of the three types of monovacancy defect can be resolved. Figure 4 shows calculated spectra for possible divacancy defects. These results provide evidence that a combination of positron lifetime (Table I) and CDBS (Figs. 2–4) measurements have the capability to identify specific vacancy related defects in Cu(In,Ga)Se<sub>2</sub> chalcogenide materials. It should be noted that positron lifetime measurements enable the determination of trapping fractions to different positron states, necessary for interpretation of CDBS spectra. They are also required to establish

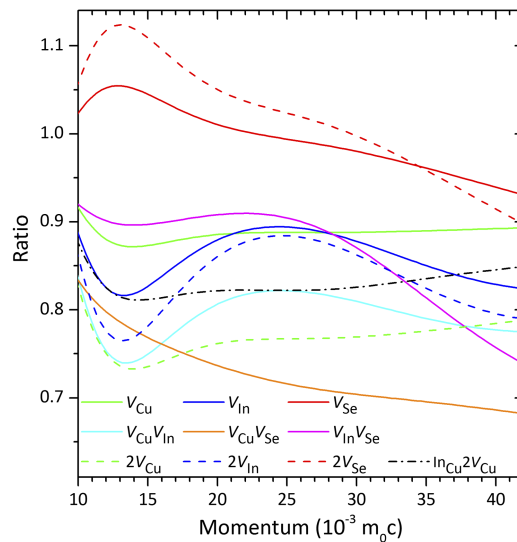


FIG. 4. Atomic superposition DFT calculated coincidence Doppler spectroscopy ratio spectra for divacancy defects in CuInSe<sub>2</sub>. The monovacancy spectra obtained using unrelaxed defect geometries are included for comparison.



unambiguously that the reference sample, required for the CDBS ratio spectra, is defect free. While this is a challenging requirement, a single bulk lifetime has been reported from a crystal CuInSe<sub>2</sub> sample.<sup>22</sup>

#### IV. CONCLUSIONS

In summary, the experimental positron lifetime results on crystal CuInSe<sub>2</sub> and Cu(In<sub>0.95</sub>Ga<sub>0.05</sub>)Se<sub>2</sub> grown by the vertical Bridgman method presented here demonstrate that vacancy defects are present with a concentration greater than the saturation trapping limit, which if a plausible defect specific trapping coefficient of  $1 \times 10^{15} \text{ s}^{-1}$  is assumed,<sup>55</sup> can be estimated to be approximately  $10^{18} \text{ cm}^{-3}$ . Two positron lifetime components were resolved with lifetime values of  $\sim 268 \text{ ps}$  and  $\sim 365 \text{ ps}$  (Table II). The mean positron lifetime was temperature independent, for both types of crystal. This suggests that the defect specific trapping coefficients for the two dominant vacancies exhibit a similar temperature dependence, and is consistent with both having the same local charge (either neutral or negative). Atomic superposition calculations are presented on a range of possible vacancy-related defects in CuInSe<sub>2</sub> and CuGaSe<sub>2</sub>, and are compared to previous reports (Tables I and III). Comparing the experimental values with the calculated positron lifetimes, the component value  $\sim 268 \text{ ps}$  is attributed to monovacancies or divacancies, and the second  $\sim 365 \text{ ps}$  lifetime to trivacancy, or possibly  $V_{\text{In}}V_{\text{Se}}$  divacancy, defects. The atomic superposition calculations also yield positron momentum distributions which provide an approximate description of the high momentum core electron regions. The resulting calculated coincidence Doppler broadening spectroscopy ratio spectra for vacancy defects in CuInSe<sub>2</sub> provide evidence that combined positron lifetime and CDBS measurements have the capability to provide specific defect identification in Cu(In,Ga)Se<sub>2</sub> chalcogenide materials.

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