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Chemical analysis using coincidence Doppler broadening and supporting first-principles theory: Applications to vacancy defects in compound semiconductors

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ABSTRACT

The Doppler broadening of the positron annihilation radiation contains information on the chemical environment of vacancy defects trapping positrons in solids. The measured signal can, for instance, reveal impurity atoms situated next to vacancies. As compared to integrated quantities such as the positron annihilation rate or the annihilation line shape parameters, the full Doppler spectrum measured in the coincidence mode contains much more useful information for defect identification. This information, however, is indirect and complementary understanding is needed to fully interpret the results. First-principles calculations are a valuable tool in the analysis of measured spectra. One can construct an atomic-scale model for a given candidate defect, calculate from first principles the corresponding Doppler spectrum, and directly compare results between experiment and theory. In this paper we discuss recent examples of successful combinations of coincidence Doppler broadening measurements and supporting first-principles calculations. These demonstrate the predictive power of state-of-the-art calculations and the usefulness of such an approach in the chemical analysis of vacancy defects.

1. Introduction

Positron annihilation spectroscopy is a powerful tool for characterizing open-volume defects in solids [1]. Open-volume defects traps are effective traps for positrons. One can, for instance, measure the positron lifetime, which correlates with sizes of the open volumes at vacancies in the sample. On the other hand, the Doppler broadening of the positron annihilation radiation reflects the momentum density of annihilating electron–positron pairs in the solid. A positron trapped at a vacancy defect is a local probe of its surrounding electronic structure. Doppler spectra measured in the coincidence mode are accurate up to high momenta, where the spectra are dominated by annihilation with core electrons. Therefore, experiments can, for example, reveal impurity atoms next to vacancies thanks to their differing core electron shells. Computational methods are a valuable tool in the analysis of positron annihilation measurements (for a review see Ref. [2]).

In most computational works focused on the identification of vacancy-type defects published to-date, only positron lifetimes have been calculated. There are some complications involved in relying on computed lifetimes only. First of all, the positron lifetime is rather insensitive to the chemical surroundings of vacancy defects, and therefore, does not often reveal impurity atoms complexed with vacancies. Secondly, one usually has to rely on relative changes in the calculated lifetime with respect to the bulk value, since getting an absolute agreement is unusual when using a genuinely parameter-free model. For instance, the computed positron bulk lifetime of ZnO varies between 137 ps [3] and 177 ps [4] depending mainly on how the difficult many-body physics involved is incorporated into the calculation, i.e., which approximations are used for the enhancement factor and electron–positron correlation energy. Modern electronic structure theory (see, for instance, Ref. [5]) strives towards predicting the properties of matter from first principles, i.e. without semi-empirical parameters. Approaches for electron–positron systems are not quite as developed yet and, unfortunately, the modeling of positron lifetimes cannot safely be argued to be at a fully predictive level. The above certainly applies as well to the modeling of momentum densities of annihilating electron–positron pairs. However, coincidence Doppler broadening spectra contain much more information on vacancy defects than measured positron lifetimes, and, most importantly, theory and numerically accurate calculations can reproduce important features in the spectra and help to correlate their presence with the defects' atomic structure.

In this article, we discuss how first-principles calculations combined with coincidence Doppler broadening experiments can be used as a powerful tool in the characterization of open-volume

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defects in solids. We focus mostly on positron studies of compound semiconductors such as the III-nitrides AlN [5] and InN [6]. Further, we discuss the importance of looking at the full coincidence Doppler spectrum since integrated line shape parameters can miss features that provide important information on the chemical surroundings of open-volume defects.

Further examples of the application of similar modeling to compound semiconductors, beyond the scope of the present article, include a study of impurity decoration of Ga vacancies in GaN [7] and the identification of substitutional Li on Zn site in n-type ZnO [3]. It is also relevant to model semiconductor nanostructures, formed, for instance, of the III-nitrides [8], where a high level of description is needed to account for effects related to the polar nature of the constituent materials, such as the large built-in electric fields in III-nitride heterostructures [9].

The article is structured as follows. In Section 2 we describe our approach based on combining modern electronic-structure methods with existing models for modeling positron annihilation in solids. Section 3 discusses recent examples of combining coincidence Doppler broadening measurements and computer modeling for identification of open-volume defects in semiconductors. Finally, Section 4 presents our summary and conclusions.

2. Computational models

Our calculations are based on the density-functional framework, and a practical limit of the two-component density functional theory for electron–positron systems [10]. Namely we assume that the positron, even if localized at an open-volume defect, does not affect the system's average electronic density $n_-(\mathbf{r})$. Furthermore, zero-positron density limits ($n_+ \to 0$) of the enhancement and electron–positron correlation energy functionals are used. The approximation can be justified by considering the positron with its screening cloud as a neutral quasiparticle which does not affect the surrounding average electron density [2]. In practice, the electronic structure and the electronic density, $n_-(\mathbf{r})$, can then be calculated first using standard electronic structure packages and neglecting the positron. Typically we use the local-density approximation (LDA) for electron–electron exchange and correlation energy. The positron's single-particle Kohn–Sham equation is then solved in the potential

$$V_+(\mathbf{r}) = -\int d\mathbf{r}' \, \frac{n_-(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - V_{\text{ext}}(\mathbf{r}) + V_{\text{corr}}(n_-(\mathbf{r})), \tag{1}$$

in which the first term is the attractive Hartree potential due to electrons, $V_{\text{ext}}(\mathbf{r})$ is the external potential due to nuclei, and $V_{\text{corr}}(n_-(\mathbf{r}))$ is the local-density approximation for the electron–positron correlation potential evaluated at the $n_+ \to 0$ limit. We use the parametrization by Boroński and Nieminen [10]. Above, the self-interaction correction has been made, i.e., for just one positron in the system the positron's Hartree self-interaction and exchange-correlation potential cancel. Once the electron and positron densities, $n_-(\mathbf{r})$ and $n_+(\mathbf{r})$, are both solved, the annihilation rate λ, the inverse of the positron lifetime τ, is calculated as

$$\lambda = \frac{1}{\tau} = \pi r_e^2 c \int d\mathbf{r} \, n_+(\mathbf{r}) n_-(\mathbf{r}) \gamma(n_-(\mathbf{r})). \tag{2}$$

Above, $\gamma(n_-(\mathbf{r}))$ is the enhancement factor taking into account the increase in the electron–positron contact density due to the screening, evaluated again in the $n_+ \to 0$ limit and within the LDA [10]. Fig. 1 shows positron density isosurfaces for a positron delocalized in a perfect lattice and a positron trapped at a monovacancy.

Within the density functional theory, the electron momentum density and related quantities such as the momentum density of annihilating electron–positron pairs cannot be calculated exactly even if the unknown exchange and correlation energy, electron–positron correlation and enhancement functionals were known exactly. Approximate formulae such as the independent-particle model (IPM) [11] have to be used. For the electron–positron system there exists several proposed enhancement schemes (see Refs. [12–14] to name but a few). Our method of choice is the simple state-dependent enhancement model by Alatalo et al. [14], in which the momentum density of annihilating electron–positron pairs is written as

$$\rho(\mathbf{p}) = \pi r_e^2 c \sum_j \gamma_j \left| \int d\mathbf{r} \, \exp(-i\mathbf{p}\cdot\mathbf{r}) \psi_+(\mathbf{r}) \psi_j(\mathbf{r}) \right|^2, \tag{3}$$

where the summation is over occupied Kohn–Sham orbitals $\psi_j(\mathbf{r})$ for the electrons, $\psi_+(\mathbf{r})$ is the positron state corresponding to the potential of Eq. (1), r_e is the electron's classical radius, c the speed of light, and the state-dependent but position and momentum independent enhancement factor $\gamma_j = \lambda_j^{\text{LDA}}/\lambda_j^{\text{IPM}}$, depends on the LDA and IPM annihilation rates corresponding to state j. Above,

$$\lambda_j^{\text{LDA}} = \pi r_e^2 c \int d\mathbf{r} \, n_+(\mathbf{r}) |\psi_j(\mathbf{r})|^2 \gamma(n_-(\mathbf{r})) \tag{4}$$

and λ_j^{IPM} is calculated by setting $\gamma \equiv 1$ in the above formula. The resulting momentum density of annihilating electron–positron pairs is projected along a chosen p_L axis to give the Doppler spectrum and convoluted with a Gaussian corresponding to the experimental resolution function.

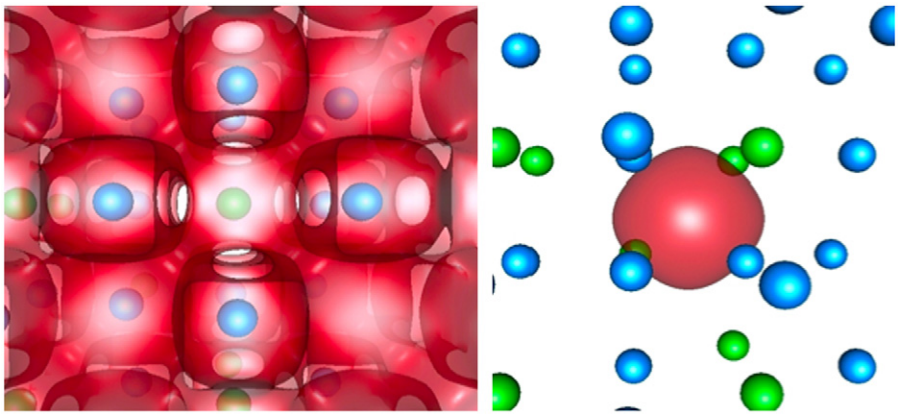

Fig. 1. Positron density isosurface in a perfect Ni_3Al lattice (left) and at a monovacancy defect (right) as predicted by calculations.