FIRST-PRINCIPLES CALCULATIONS OF POSITRON ANNIHILATION IN SOLIDS

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ABSTRACT

We present first-principles approaches based on density functional theory for calculating positron states and annihilation characteristics in condensed matter. The treatment of the electron-positron correlation effects (the enhancement of the electron density at the positron with respect to mean-field density) is shown to play a crucial role when calculating the annihilation rates. A generalized gradient approximation (GGA) takes the strong inhomogeneities of the electron density in the ion core region into account and reproduces well the experimental total annihilation rates (inverses of the positron lifetimes) by suppressing the rates given by a local density approximation (LDA). The GGA combined with an electron-state-dependent enhancement scheme gives a good description for the momentum distributions of the annihilating positron-electron pairs reproducing accurately the trends observed in the angular correlation (ACAR) or Doppler broadening measurements of the annihilation radiation. The combination of the present positron lifetime and momentum density calculations with the corresponding measurements yields a unique tool for defect identification. Especially, the investigation of various vacancy-type defects in semiconductors able to trap positrons will be an important field for these methods. We will show that the identification of vacancy-impurity complexes in highly n-Type Si and the study of the SiO$_2$/Si interface are particularly interesting applications.

INTRODUCTION

Lattices of crystalline materials are not perfect on the atomic scale since point defects always exist. Defects can dramatically change physical properties of materials, even if their concentration is very low. For instance, in semiconductors defects may increase absorption or emission of light in radiative recombination processes. Experimental methods based on positron annihilation [1, 2] can identify point defects in semiconductors in concentrations as low as 0.1 ppm. Because the energy-loss cross sections for positrons are high, they slow down to thermal energies before annihilating, even though they are formed with high energies in beta decay. The positron lifetimes in solids are typically about 100 - 300 ps. If the positron is localized in a vacancy-type defect, its lifetime increases from that of an extended positron state. Also the total momentum of the annihilation photon gives useful (chemical) information about the environment where the annihilation occurs. Thus these changes in the positron annihilation characteristics make the positron annihilation spectroscopies powerful to study defects in semiconductors from the viewpoint of material science as well as from that of industrial applications. The goal of our work is to develop computational approaches for predicting electron and positron states and annihilation characteristics in materials in order to support the experimental research of defects by different positron annihilation methods. We have have developed models within Density Functional Theory (DFT).
METHOD

DFT solves for the electronic structure of a condensed matter system in its ground state so that the electron density $\rho^-$ is the basic quantity [3]. The DFT can be generalized to positron-electron systems by including the positron density $\rho^+$ as well; it is then called as the 2-component DFT [2, 4]. As a consequence of the Hohenberg-Kohn theorem [3] the ground-state value of any operator $\hat{o}$ is a functional of the electron and positron densities denoted by $O[\rho^-, \rho^+]$. It can be shown [3] that

$$O[\rho^-, \rho^+] = O_0[\rho^-, \rho^+] + \frac{d}{d\lambda} E_{xc}[\rho^-, \rho^+](\lambda), \quad (1)$$

where $O_0[\rho^-, \rho^+]$ is the expectation value of $\hat{o}$ for a system of noninteracting fermions moving in the effective field provided by the Kohn-Sham formalism [3], $E_{xc}$ is the exchange-correlation energy functional and $\lambda$ is a scalar coupling parameter for the operator $\hat{o}$. This general expression for $O[\rho^-, \rho^+]$ generalizes the Lam-Platzman theorem [5] and provides a formal scheme to extract positron annihilation characteristics from the 2-component DFT.

The Local Density Approximation (LDA) was the first implementation of the DFT [2, 3] and it provides an explicit formula for $E_{xc}$. The more recent Generalized Gradient Correction (GGA) gives a systematic improvement for first-principles electronic calculations with respect to the LDA [6]. The GGA is even more successful for positron-electron correlation effects in solids when positron lifetimes, energetics, and momentum distributions of the annihilating electron-positron pairs are considered [7-10].

RESULTS

The positron affinity is an energy quantity defined by $A^+ = \mu^- + \mu^+$, where $\mu^-$ and $\mu^+$ are the electron and positron chemical potentials, respectively [11]. The affinity can be measured by positron emission spectroscopy [12] and the comparison of measured and calculated values for different materials is a good test for exchange-correlation functionals. The LDA shows a clear tendency to overestimate the magnitude of $A^+$ [7]. This overestimation can be traced back to the screening effects. In the GGA, the value of $A^+$ is improved with respect to experiment by reducing the screening charge. In Fig. 1 we give the calculated positron affinities within LDA and GGA to the corresponding experimental values for several metals.

In the case of a semiconductor $\mu^-$ is taken from the position of the top of the valence band. Kuriplach et al. [13] calculated $A^+$ for different polytypes of SiC and showed that the GGA agrees better with the experimental values than the LDA. However these experimental data are still plagued with significant error bars of about 0.5 eV. Therefore more experimental work is necessary to judge the accuracy of the present GGA in semiconductors. One should also note that the computed $A^+$ values may also depend significantly on the wavefunction basis set, i.e. whether, for example, the atomic-sphere approximation [13] or the pseudopotential-plane-wave approach [14] is used.

In a solid, the shape of the screening cloud at the positron resembles that of a positronium atom ($Ps$). The positron-electron contact density, which is remarkably higher than the unperturbed electron density, determines the positron lifetime. The ratio is called the enhancement factor $\gamma$. In the LDA, the local positron contact density is treated as a function of the local electron density. The LDA underestimates systematically the positron lifetime in real materials while for the GGA, the agreement with the experiment is excellent as...
Figure 1: Positron affinities for several metals. The solid and open circles give the GGA and LDA results as a function of the experimental ones, respectively. The solid line corresponds to the perfect agreement between the theoretical and experimental results from refs. [12].

shown in Fig. 2 [7, 8]. For this comparison we have taken an LDA enhancement factor $\gamma$ [7] which is consistent with the LDA potential given by Boronski and Nieminen [4]. Indeed one expects that the strong electric field due to the inhomogeneity suppresses the electron-positron correlations in the same way as the Stark effect decreases the contact density for the $Ps$ atom. In the GGA [7, 8], the contact density depends also on the density gradient and the gradient correction reduces the electron-positron correlation. The reduction of the enhancement factor due to the GGA is not large in the interstitial regions in metals or semiconductors. On the contrary, the GGA reduces strongly the enhancement factor in the regions of core and semicore electrons.

Very large deviations between theoretical and experimental lifetimes are observed particularly in II-VI compounds semiconductors, since the LDA overestimates the magnitude of the positron annihilation rate with the d electrons. Moreover, in the LDA framework, one has to introduce for semiconductors and insulators a semiempirical correction based on the dielectric constant in order to describe well the positron lifetime $\Gamma$. This correction is not necessary in the GGA. Finally, Ishibashi has shown that the GGA reproduces the experimental values much better than the LDA even for the low-electron-density systems such as the molecular crystals of C$_{60}$, TTF-TCNQ and (BEDT-TTF)$_2$Cu(NCS)$_2$ [13]. Therefore the GGA can be safely applied when identifying vacancy-type defects in semiconductors.

The Doppler broadening technique [9] and the two-dimensional angular correlation of the annihilation radiation (2D-ACAR) [16] are powerful momentum-density spectroscopies for identifying defects in semiconductors. In the scheme described in Ref. [10] the theoretical momentum distribution is obtained from the shapes which are determined within the independent particle model for each occupied electron state and weighted by its anni-
Figure 2: Positron lifetimes for perfect solid lattices. The solid and open circles give the GGA and LDA results as a function of the experimental ones, respectively. The solid line corresponds to the perfect agreement between the theoretical and experimental results.

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of this phase is not yet understood. An interesting hypothesis by Altshuler and Maslov [20] includes temperature- and field-dependent filling and emptying of charged hole traps unavoidably introduced during the device fabrication at the interface. We are planning to check this hypothesis by comparing the positron annihilation spectroscopy with our theoretical predictions. Preliminary results by Kauppinen et al. [21] indeed suggest that high concentrations of open-volume defects, probably divacancies, exist near the interface.

CONCLUSION

We have shown that the scheme based on measuring and calculating positron lifetime and momentum distributions is a reliable tool to analyze materials properties. The study of defect-free bulk samples gives credence to use the GGA for the electron-positron correlation effects. The localized positron states at defects have also been found well described by the GGA. By performing model calculations one can also propose new experiments to identify point defects in semiconductors.

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