Hyperfine interactions in muonium–impurity complexes in silicon

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The properties of paramagnetic complexes formed by muonium located near acceptor and donor impurities in silicon are calculated using the quantum chemical methods. The calculated data are compared to the experimentally observed characteristics of “normal” and “anomalous” muonium centers.

At present great interest is aroused by problems concerned with the behaviour of hydrogen in semiconductors. One of the methods providing the necessary information is the μSR method [1] enabling one to study properties of muonium \( \text{Mu} = \mu^+ e^- \) which is a light unstable isotope of atomic hydrogen H. At the same time, only recently [2] it has been proved experimentally that behaviour of Mu in semiconductors is similar to that of H: as it turned out [3], the EPR center Si-AA9 detected in Si [2] is a hydrogen-bearing analogue of the so-called “anomalous” muonium (Mu*), i.e. a Mu state existing in semiconductors along with the “normal” muonium (Mu') and diamagnetic (\( \mu^+ \)) state [1].

Based on the analogy observed in Mu and H behaviour, it is quite natural to assume that muonium in impurity semiconductors can form Mu–impurity complexes similar to those which are formed by H upon passivation of donors and acceptors [4]. The detection and investigation of such complexes would make it possible to extract important information about the mechanisms of impurity passivation. However, the complexes indicated being at \( T \approx 300 \) K in a neutral charge state, as are H–impurity type complexes, will be diamagnetic. Therefore, it will
prove impossible to distinguish them from other diamagnetic states, such as, for example, free $\mu^+$, by means of the traditional $\mu$SR-experiments. However, if we change the charge state of neutral complexes by unity (using, for instance, illumination or altering the position of the Fermi level through the introduction of the corresponding compensation centers) thus rendering them paramagnetic, it will become possible to identify these states by measuring the corresponding hyperfine interaction constant (HFI). Note that the positive paramagnetic complexes of the type $\mu$-acceptor (donor) can also be formed at low temperatures $T < 100$ K due to the capture of a diffusing $\mu^+$ by a neutral acceptor (donor). So it seems timely to carry out quantum chemical calculations of the electronic structure of muonium like paramagnetic complexes $\mu$-impurity, whose existence in semiconductors is possible under certain conditions. (Experimental results [5] admit that H–P positive complexes exist in Si.)

In the present paper we calculate in cluster approximation the electronic structure of positive complexes formed by muonium located at different sites of the silicon crystal lattice near the acceptor (B, Al) and donor (P, As) impurities using the quantum chemical INDO (intermediate neglect of differential overlap) method [6]. Use is made of the SPIN-HAMILTONIAN programme [7], allowing one to obtain both the HFI tensor and the muonium electronic g-tensor in the framework of accepted approximations. The HFI constants and g-tensor are calculated in the equilibrium geometry of the clusters $(\text{MuXSi}_7\text{H}_{18})^{1+}$ ($X = \text{B, Al, P, As}$), centered at the BC site between the substitutional atom $X$ and the Si lattice atom. The $X$–Si bond direction coincided with the $\langle 111 \rangle$ crystallographic axis. In the calculations we accounted for the symmetric relaxation of the coordinate sphere being the nearest one to atom $X$. The resulting $X$–Si bond length turned out to be close to the sums of the covalent radii of the Si and $X$ atoms. As in ref. [8] where the H-impurity neutral complexes in Si are treated, we consider here the following possible sites of Mu localization: AB-point of Si, BC-point and AB-point of $X$. Equilibrium positions of Mu were found by minimizing the total energy of the corresponding clusters.

A comparative analysis of the results and data given in refs. [8,9] has revealed that the equilibrium positions of the Mu and $X$ atoms undergo slight changes with varying charge states of the $\mu$–$X$ complexes. Besides, in complexes which contain acceptors the most energetically favourable equilibrium positions for Mu are those wherein Mu is localized at BC-sites. Whereas for complexes containing donors, the deepest minimum of the cluster total energy corresponds to the Mu location at AB-sites of Si. Therefore, the transformation of the above neutral diamagnetic complex to a paramagnetic state (e.g. by illuminating the samples) should result in neither complex destruction, nor a considerable change of its equilibrium geometry.

The principal values of Mu HFI- and g-tensors axially symmetric with respect to a $\langle 111 \rangle$ axis in possible equilibrium positions for the $(\text{MuXSi}_7\text{H}_{18})^{1+}$ clusters are given in table 1. In addition to the principal values of the HFI tensors, table 1