

Elementary model for anomalous muonium in silicon, germanium, and diamond

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The hyperfine interaction constants in anomalous muonium are calculated for several semiconductors in the model of a complex consisting of a diamagnetic molecule plus an unpaired electron. The exchange interaction in the system is taken into account. The calculated results show that the complex forms in a monovacancy of the corresponding crystal lattice.

In contrast with normal muonium, Mu (a bound state of the μ^+e^- system), for which the hyperfine interaction (HFI) of the muon with the electron is isotropic, anomalous muonium, Mu^* , which forms in several semiconducting single crystals (silicon,¹ germanium,² and diamond³), exhibits an obviously anisotropic HFI. In the absence of an external field, the Hamiltonian for the HFI in Mu^* is^{1,4} $H = A_{\perp}(I_x S_x + I_y S_y) + A_{\parallel} I_z S_z$ (I and S are the spin operators of μ^+e^- , and A_{\perp} and A_{\parallel} are the HFI constants) and reflects the axial symmetry of the system, with an axis running parallel to one of the $\langle 111 \rangle$ directions of the corresponding lattice. For our purposes below, it is more convenient to choose a different set of HFI constants: A_s and A_p , which represent the contributions of the contact dipole component and the magnetic dipole component to the total HFI and which are related to A_{\perp} , A_{\parallel} (introduced above) by $A_s = 1/3(A_{\parallel} + 2A_{\perp})$ and $A_p = 1/3(A_{\parallel} - A_{\perp})$. Experiments yield the following values (in megahertz) for these constants: $A_s = \pm 67$ (Si), ± 96 (Ge), -206 (diamond), $A_p = \pm 25$ (Si), ± 35 (Ge), and 187 (diamond). In other words, these values run one or two orders of magnitude lower than the HFI constants for Mu in a vacuum (4463 MHz). Experiments reveal the signs of the constants A_s and A_p unambiguously only in the case of diamond (on the basis of the conversion $\text{Mu} \rightarrow \text{Mu}^*$; see Ref. 5, for example).

Our purpose in the present study was to seek a configuration which reflects the basic properties of Mu^* , including the anisotropy of the system and the values of the constants $A_{s,p}$, with their signs. If the model is to be universally applicable, the signs of the constants must be the same for all three objects, so that at this point we adopt $A_s = -67$ (Si), -96 (Ge), $A_p = 25$ (Si), 35 (Ge).

We begin our analysis with the model proposed in Ref. 6 for Mu^* in silicon (Fig. 1): a complex consisting of a diamagnetic Si–Mu molecule (which includes normal muonium, Mu, and which forms at one site Si_1 of the silicon lattice) and an unpaired electron e^- , which is localized at another site, Si_2 , near Si_1 . The spin of the muon in this system interacts (in the zeroth approximation) only with the spin of the “foreign” electron (the unpaired electron at Si_2), while the spin of the muonium’s own electron is paired with a valence electron of the Si_1 atom and does not participate in the HFI.

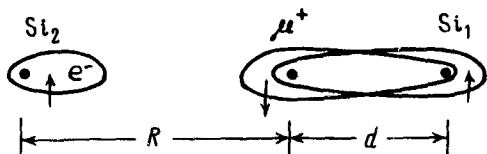


FIG. 1. Silicon. General view of the complex. The exchange polarization shifts the valence electrons to the right or the left. The orientations of the spins are shown by the arrows.

Even in the next approximation, however, we should consider the exchange polarization of a pair of valence electrons of the molecule under the influence of the unpaired electron. In this case (Fig. 1), an unpaired electron, whose spin is assumed, for definiteness, to be pointed "upward," attracts to itself that valence electron whose spin is pointed "downward," and it repels the second valence electron, with a spin pointed upward. This process leads to a nonzero spin density of the electrons of the valence pairs of the muon, so that in this system, in addition to the "direct" HFI of the muon with the unpaired electron (the constants A_s , A_p), we should also consider the "induced" HFI (the constants δA_s , δA_p) of the muon with the induced spin density. The resultant HFI of the muon with all three electrons is determined by the renormalized constants $\tilde{A}_s = A_s + \delta A_s$, $\tilde{A}_p = A_p + \delta A_p$. Further calculations show that the inequality $|\delta A_p| \ll |A_p|$ holds in all cases, so we adopt $\tilde{A}_p \cong A_p$. In contrast, the values of δA_s turn out to be comparable in magnitude to A_s , and when the μ^+ is well-separated from Si_2 (2–3 Å) the value of \tilde{A}_s is determined by the value of δA_s almost completely. This circumstance explains the negative sign of \tilde{A}_s (the sign of the spin density of the valence electron at the muon).

A specific calculation of the HFI constants (reported in detail in Ref. 7) requires specifying the wave functions of the unpaired and valence electrons. As atomic orbitals we selected the $1s$ orbitals for Mu and the sp^3 hybrids for valence electrons in Si, Ge, and C (diamond). As their radial parts we selected Slater orbitals.⁸ The values of δA_s are determined by the "configurational-interaction" method⁹; as excitations we choose "antibinding" orbitals of the molecule (in accordance with the method of Ref. 10). The lengths (d) of the Si–Mu, Ge–Mu, and C–Mu molecules are chosen in each case to be equal to the lengths of the corresponding bonds: Si–H (1.47 Å), Ge–H (1.53 Å), and C–H (1.09 Å).

The results calculated for A_p , A_s , δA_s , and \tilde{A}_s as functions of the distance R (an adjustable parameter), the distance from the μ^+ to Si_2 , are shown for silicon in Fig. 2. A criterion for choosing values of R corresponding to the actual sizes of the complex is the relation $A_p = A_p^e$, provided that the relation $\tilde{A}_s \cong A_s^e$ holds for the same values of R . It can be seen from Fig. 2 that in using this method we find several distinct values of R (and the same is true in the cases of germanium and diamond) which satisfy this criterion. The introduction of the auxiliary condition $R \geq d$ (otherwise, a molecule could not form), however, eliminates this ambiguity, and in each case we find a single value of R . These results are (in atomic units) 5.1 (Si), 4.7 (Ge), and 3.6 (diamond). The calculated values of \tilde{A}_s for the same values of R are (in megahertz) –43 (Si), –44 (Ge), and –66 (diamond).

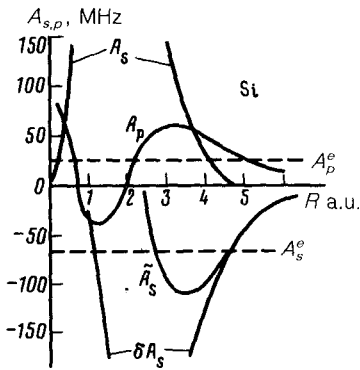


FIG. 2. Silicon. The calculated constants of the hyperfine interaction (in megahertz) versus the distance R (in atomic units; 1 a.u. = 0.529 Å). The dashed lines are experimental values $A_{s,p}^e$.

The values found for R in this way can be explained in a natural way by assuming that in each case (Si, Ge, and diamond) the complex lies inside a (neutral) monovacancy of the corresponding (rigid) lattice. In this case the model forms at one of the four vertices of the vacancy, with the muon facing the center of the vacancy; R corresponds to the distance (R_v) from the muon to one of the three other vertices. Knowing the lattice constant and the length of the molecule, we can easily find R_v . The results are (in atomic units) 5.2 (Si), 5.5 (Ge), and 3.3 (diamond).

The mechanism for the hyperfine interaction in a model for Mu^* altered to this extent requires further discussion, since there are three ruptured bonds in place of the single unpaired electron in the original model for Mu^* . Nevertheless, since the total spin of the system of three electrons in its lowest state is $1/2$, two of the three ruptured bonds with opposite spin orientations can pair up, so that the spin of only one electron remains "free." In Ref. 7, I analyzed two versions of this model. In a "dynamic" version, the spin of each of the three ruptured bonds becomes in turn the free spin (the spins of the two other ruptured bonds also pair up in turn). The frequency of this process is $\sim 10^{13} \text{ s}^{-1}$, i.e., $\gg A_{s,p}$, and the muon "sees" an unpaired electron which is smeared uniformly over three vertices of the vacancy. The symmetry axis of the complex in this case is the direction in which the molecule is oriented, i.e., one of the $\langle 111 \rangle$ directions of the lattice. In many ways, this version of the model is similar to the Mu^* model examined in Ref. 11: a corresponding complex inside a doubly charged monovacancy. In a "static" version, the unpaired electron remains at all times at the same vertex of the vacancy, and the two other ruptured bonds are constantly paired to each other. In this version, the direction from the muon to the unpaired electron acquires a real meaning. This direction, however, does not coincide with any of the lattice $\langle 111 \rangle$ directions. It was shown in Ref. 7 that in this case there should be a doublet splitting of the precession frequencies of Mu^* in an external field $H \gtrsim 1 \text{ kG}$ [we do not rule out the possibility that this is the explanation for the doublet frequency splitting, $\sim 5 \text{ MHz}$, which is observed in Ge (Ref. 2)]. Finally, we note that in all cases the question of the formation of a complex in a monovacancy remains open.

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