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necessary to fold the instrument function with a core-level Lorentzian broadening and then with the unoccupied DOS. This was done. It only makes a difference of a few hundred millielectronvolts in the assignment of E_F for Ni. The use of this three-point calibration procedure allows us to rule out effects of nonlinearities in comparison of our XPS and XAS data and be confident that the two experimental BE scales are aligned to better than 300 meV. This error is much less than the size of the effects described here.

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Self-Consistent-Field Investigation of Location and Hyperfine Interaction of Muonium in Diamond

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(Received 21 May 1982; revised manuscript received 10 December 1982)

With use of an unrestricted Hartree-Fock self-consistent-field cluster approach, the potential experienced by a muon in diamond has been investigated. The results strongly indicate that normal muonium is localized in the tetrahedral interstitial space. By using the calculated spin density and averaging it explicitly over the vibrational motion of the muon a quantitative explanation is obtained for the observed reduction of the hyperfine field as compared to free muonium.

PACS numbers: 71.70.Jp, 71.55.Fr, 76.90.+d, 78.50.Ec

Hyperfine data from recent experiments using the muon-spin-rotation technique¹ in group-IV semiconductors^{2,3} are found to have the following

interesting features. (a) The hyperfine fields associated with normal muonium in these systems^{3,4} are significantly reduced from the vacuum hyper-

fine field and exhibit an irregular trend of decrease from diamond to silicon (Si) and increase from Si to germanium (Ge). (b) An anomalous muonium level with a rather weak but anisotropic hyperfine interaction and a similar irregular trend is observed in all three systems.^{4,5} The exact location of the normal and anomalous muonium systems has not yet been established.

The earliest theoretical investigation⁶ on the hyperfine interaction of normal muonium in semiconductors utilized a dielectric treatment and was able to explain the observed feature^{2,3} of reduction of the hyperfine fields in Si and Ge as compared to free muonium. However, when applied to diamond⁴ it led to a hyperfine field substantially smaller than in Si, in contradiction with experiment.^{3,4} This situation, as well as the results of an approximate molecular-orbital calculation by the semiempirical self-consistent-charge extended Hückel procedure on Si and Ge,⁷ has led to the proposition in the literature⁴ that a first-principles procedure explicitly incorporating the effects of the electron distributions of the neighboring atoms was needed to understand the experimental results and explore the location of the muonium.

There are two possible avenues for including the effects of the electronic distribution of the neighboring atoms on the muonium atom, one being to use⁸ the results of the electronic distribution from band calculations in the host lattice and compute the potential around the muonium site due to this distribution. The second way, which is in keeping with recent emphasis⁹ on the use of localized approximations for studying local properties like the hyperfine interaction, is a self-consistent-field Hartree-Fock cluster approach. In the present work we have adopted the latter approach using currently developed methods for handling such calculations in a practicable manner,¹ studying for the first time the electronic structures and energies associated with (1s-like) muonium at different positions in diamond, using an unrestricted Hartree-Fock (UHF) molecular-orbital approach for a cluster consisting of the muonium and 26 atoms surrounding it as shown in Fig. 1.

The UHF cluster approach utilized here has provided a first-principles determination of both the spin density seen by the muon as a function of its position and the potential that determines its location and motion. The latter provides the definitive conclusion that the muon is located in the tetrahedral region and not the hexagonal one,

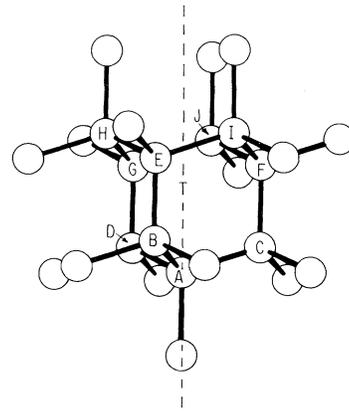


FIG. 1. Cluster used in present work. A through J are carbon atoms, and the rest are hydrogen atoms. T represents the tetrahedral interstitial site.

and using the spin-density curve and vibrational wave function for the calculated potential, we are able to obtain a vibrationally averaged value of the hyperfine constant for muonium in essential agreement with experiment.⁴ The UHF procedure used here has the merit that within the framework of the cluster model it directly includes important effects such as Pauli repulsion between the muonium electron and other electrons in the lattice and the spin-polarization mechanism¹⁰ which has an important influence on the spin density. Further, the results of the present analysis allow valuable insights into the origin of the trend in the hyperfine fields in diamond, silicon, and germanium.

In the cluster (Fig. 1) of 27 atoms used in our work, the neighbors of muonium were host carbon atoms, the dangling bonds being saturated by hydrogen atoms. This cluster size was considered adequate, since a smaller cluster of fifteen atoms yielded energy and spin-density curves in the $\langle 111 \rangle$ direction in better than 10% agreement with the chosen larger cluster.

The electronic energy levels and wave functions are obtained by use of the variational UHF procedure,¹⁰ with the molecular-orbital wave functions Ψ_μ expanded as

$$\Psi_\mu = \sum_i C_{\mu i} \varphi_i, \quad (1)$$

the atomic orbitals φ_i being constructed from Gaussian orbital functions¹¹ which permit analytic evaluation of the one-electron and two-electron integrals involved. The summation in i was carried out over the 1s states of the muonium and the terminal hydrogen atoms in the cluster and the 1s, 2s, and 2p states of the carbon atoms.

For each of these basis functions, the STO-3G approximation¹¹ was utilized, each atomic orbital being expressed in terms of three Gaussian functions. The reliability of this choice of basis set for the calculation of spin densities at nuclei has been tested by comparison of results with this choice as well as with more extensive basis sets for a number of small molecular systems to be discussed elsewhere.¹²

In Fig. 2, the calculated total energy of the cluster with reference to that at T , the tetrahedral interstitial site, has been plotted as a function of muonium position along the $\langle 111 \rangle$ direction. The potential curve in Fig. 2 is symmetrical about the hexagonal site H , and has the following notable features. The potential closely resembles that of a harmonic oscillator around T and has a minimum at this point. We have examined the force on the muon at T and neighboring points around it both on the $\langle 111 \rangle$ axis and in directions transverse to it using Hellman-Feynman theorem¹³ and found that the force vanishes only at T , confirming that the potential has an absolute minimum at this point. However, as one moves from T towards carbon atom A , a kink appears in the potential at a distance from A close to the C-H bond length, indicating that the muonium attempts to bond covalently with A . But it is unable to form a C-H bond of normal strength, because of competition from other carbon atoms to which A is bonded, as well as the influence on the muonium of its other carbon neighbors.

The potential has a maximum at the hexagonal site H , indicating that the muon would avoid this region. Also, the ground-state energy for the three-dimensional harmonic oscillator around T is 0.48 eV, which is significantly below the

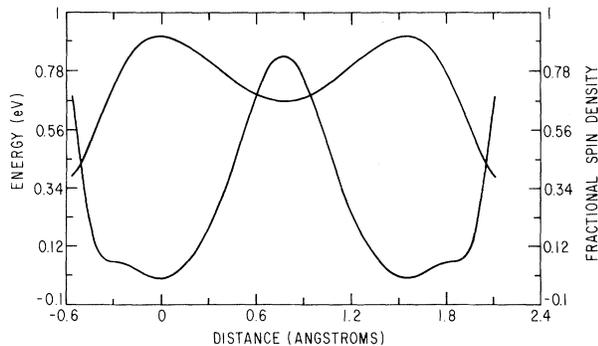


FIG. 2. Variation of total energy of 27-atom cluster and fractional spin density f at muon site with muonium position. Zero of energy is taken at tetrahedral site T .

maximum of the potential (0.83 eV) at H . Further, the overlap of the ground-state harmonic oscillator wave functions in the two equivalent tetrahedral regions on either side of H (Fig. 2) is found to be of the order of only 10^{-3} , too small for any significant tunneling to occur. Additionally, for classical passage over the barrier, one requires an excitation above the potential at H , that is 0.35 eV, substantially larger than kT at the maximum temperature of measurement⁴ (150 K). Thus one can safely say that the muon will be trapped in one of the tetrahedral regions in diamond.

The spin density $\rho(R)$ at different muon positions, obtained from the UHF electronic wave functions, was found to have contributions from both unpaired and paired spin orbitals, the latter making a 25% contribution, which would have been missed in a restricted Hartree-Fock calculation. The fractional spin density $f(R) = \rho(R) / \rho_{\text{vac}}$ (where $\rho_{\text{vac}} = 1/\pi = 0.318 a_0^{-3}$), in Fig. 2, is maximum at T and decreases in either direction, in a more pronounced manner as one moves towards A . The contrasting feature of decrease in f and increase in energy (Fig. 2) as one moves away from T is a likely consequence of the increased bonding between the muon and neighboring carbon atoms which reduces f , but leads to an increase in total energy due to the weakening of the bonding of the carbon atoms with their other neighbors.

To obtain the vibrationally averaged spin density ρ_{av} at the muon, one has to evaluate the three-dimensional integral $\int |\Psi_v(\vec{R})|^2 \rho(\vec{R}) d^3R$, v referring here to the ground vibrational state. The evaluation of this integral can be simplified by the following considerations. First, from vibrational averaging over one dimension in the $\langle 111 \rangle$ direction, it was found that the major contribution arose from the neighborhood of T , where the potential had primarily a harmonic oscillator form KX^2 which could be further improved by adding a small anharmonic term αX^3 . Secondly, the three-dimensional vibrational motion of the muon is expected to be well represented by that of a molecule with T_d symmetry¹⁴ with the symmetry axes TA , TE , TF , and TG (displacement vectors in these directions being \vec{r}_1 , \vec{r}_2 , \vec{r}_3 , and \vec{r}_4 , respectively) in Fig. 1. Of the corresponding symmetry coordinates $\vec{S}_1 = \frac{1}{2}(\vec{r}_1 + \vec{r}_2 - \vec{r}_3 - \vec{r}_4)$, $\vec{S}_2 = \frac{1}{2}(\vec{r}_1 - \vec{r}_2 + \vec{r}_3 - \vec{r}_4)$, $\vec{S}_3 = \frac{1}{2}(\vec{r}_1 - \vec{r}_2 - \vec{r}_3 + \vec{r}_4)$, and $\vec{S}_4 = \frac{1}{2}(\vec{r}_1 + \vec{r}_2 + \vec{r}_3 + \vec{r}_4)$, the last one is redundant and the vibrational wave function is of the triply degenerate F type,¹⁴ $\Psi_v(\vec{S}_1) \Psi_v(\vec{S}_2) \Psi_v(\vec{S}_3)$. Thus ρ_{av}

can be reexpressed as

$$\rho_{av} = \int |\Psi_v(s_1)|^2 |\Psi_v(s_2)|^2 |\Psi_v(s_3)|^2 \times \rho(s_1, s_2, s_3) ds_1 ds_2 ds_3. \quad (2)$$

The vibrational wave functions $\Psi_v(s_i)$ were taken as the ground-state wave functions in the potentials $V(s_i) = K's_i^2 + \alpha's_i^3$, with $K' = \frac{3}{4}K$ and $\alpha' = \frac{3}{8}\alpha$, and were obtained variationally by taking the admixture of ground- and first-excited-state harmonic-oscillator wave functions. The spin-density function $\rho(s_1, s_2, s_3)$ was also found to be well fitted by the expression $\rho_0 + \sum_i (\beta S_i^2 + \gamma S_i^3)$, ρ_0 referring to the spin density at T .

Using this procedure we obtained ρ_{av} of about 0.75 of the free hydrogen-atom spin density, composed of 0.90 from ρ_0 (which would be the result if no vibrational averaging was applied), and contributions from the quadratic and cubic terms in ρ of -0.18 and $+0.03$, respectively. This result and the fact that ρ_{av} was essentially unchanged when the cubic term in the potential was dropped indicates that higher-order terms in the potential and spin density would not affect ρ_{av} significantly. Our result for $f_{av} = 0.75$ is within 10% of the experimental value in diamond⁴ of 0.829. The small remaining difference could perhaps be reduced through the incorporation of correlation effects beyond the Hartree-Fock approach which are rather difficult to handle in an *ab initio* manner in molecular cluster calculations.

The potential and spin-density curves in Fig. 2 provide a possible explanation of the observed trend of the muon hyperfine interaction in going from diamond to silicon to germanium. Thus, had the kink in the potential curve close to a C-H bond distance away from A been more pronounced and led to a deeper minimum than at T , the muon would have been trapped here and experienced a substantially smaller spin density, and a vibrational frequency comparable to the single-bond C-H frequency would have been observed for hydrogen in diamond. This situation is precluded by the shallowness of the kink in Fig. 2 as compared to the minimum of the T site, which is probably a result of the competition between the four carbon atoms surrounding the interstitial region for bonding with the muonium. The availability of larger interstitial spaces in silicon and germanium may well tip the balance in favor of bonding to a single host atom rather than equal bonding to four of them as occurs at the T site. If this were to happen, one would then have explanations for the smaller spin densities^{4,5} in silicon and germanium as compared to diamond,

the occurrence¹⁵ of an infrared frequency for hydrogen in silicon comparable to that for normal Si-H bonds, and the off-center trapping of deuterium in silicon revealed by channeling experiments.¹⁶

In summary, the present first-principles self-consistent-field Hartree-Fock investigation has provided both a definite conclusion regarding the location of the muon and a satisfactory explanation of the experimentally observed hyperfine constant in diamond. The success of the present work suggests that the procedure adopted here should be appropriate for attempting to explain the observed trends in the normal muonium hyperfine constants in the heavier semiconductors. Also, the results of the present work indicate that normal muonium is not localized in the hexagonal region. However, it is possible that the observed anomalous muonium state,⁴ with its weak hyperfine interaction, could be associated with a $2p$ -like state of a muonium which might be localized in the hexagonal space.¹⁷ But since the $2p$ state is expected to be more diffuse, it could produce significant lattice relaxation involving displacements of the host atoms. While the cluster approach could be applied to an investigation of this case, it is expected to be substantially more time consuming than the present work.

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Statics and Dynamics of a Two-Dimensional Ising Spin-Glass Model

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(Received 28 January 1983)

The temperature and field dependence of spatial correlations and relaxation times are investigated in detail by Monte Carlo simulations for a two-dimensional Ising spin-glass model. There is no transition, but, in zero field, barrier heights and correlation range increase smoothly at low temperatures. This increase does not seem to be fast enough to explain experiments. In a field, barrier heights and the correlation length tend to a finite limit as $T \rightarrow 0$. Points in the h - T plane with constant relaxation time satisfy $T(h) - T(0) \propto h^{2/3}$ at moderately low temperatures.

PACS numbers: 75.10.Hk, 05.50.+q, 64.60.Cn

There are several calculations¹ on spin-glass models with short-range interactions which predict a lower critical dimension (LCD) of 4. Consequently there should be no spin-glass transition in three dimensions and the infinite-range Sherrington-Kirkpatrick² (SK) model, which does have a transition, should be inappropriate for explaining experiments. It is therefore surprising that the following experimental results are reasonably well described by the SK model: (a) There is a dramatic increase^{3,4} in the nonlinear susceptibility, χ_{nl} , in the same region of temperature, T , as the cusp in the linear susceptibility. χ_{nl} diverges in the SK model but remains finite if there is no transition. (b) There is evidence^{5,6} for a "transition line" in the h - T plane (h is a uniform field), similar to the Almeida-Thouless⁷ line for the SK model. Even the power-law variation $T_c(h) - T_c(0) \propto h^{2/3}$, for small h , predicted by Almeida and Thouless, seems to be found experimentally. (c) For certain materials at least, the temperature of the susceptibility peak varies very little with frequency,⁸ as is natural in the phase-transition hypothesis. However, a much larger variation is predicted by the alternative

picture of "gradual freezing."⁹

These results suggest that either the prediction of an LCD equal to 4 is wrong or correlation lengths, and relaxation times, while not strictly diverging, increase considerably over a narrow temperature range as a result of cooperative effects between the spins. In order to decide which of these two alternatives is correct one needs to know *quantitatively* the range of correlations in space and time as functions of h and T . While the spatial extent of correlations with $h=0$ has been discussed,^{1,10} albeit on somewhat small lattices, virtually¹¹ no precise results on relaxation times have been given, and little is known about the effect of a magnetic field. Here I start to fill in this important gap by reporting results of detailed Monte Carlo studies of the Edwards-Anderson model with Ising spins on fairly large square lattices of size $N = L \times L$, where $L = 68$ and 128 . The Hamiltonian is given by

$$H = - \sum_{\langle ij \rangle} J_{ij} S_i S_j - h \sum_i S_i, \quad (1)$$

where $S_i = \pm 1$, $i = 1, \dots, N$, and J_{ij} is a nearest-neighbor interaction taking values ± 1 with equal