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A REVIEW OF THE EXPERIMENTAL RESULTS ON IMPURITY CENTERS IN ELEMENTAL SEMICONDUCTORS OBTAINED BY μSR AND OTHER TECHNIQUES

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ABSTRACT

I briefly review selected electron paramagnetic resonance studies of defect centers in group IV semiconductors. I point out features of this research which are useful in analyzing the nature of normal and anomalous muonium (Mu and Mu^*) in these crystals. A moderately specific model of Mu and Mu^* is presented and compared to studies of hydrogen in silicon and germanium.

More is known about defect centers in silicon than about centers in any other crystal. Much of this has come from electron paramagnetic resonance (EPR) studies[1]. Consequently, it is reasonable to ask whether this vast store of information can be of value in establishing models for the normal and anomalous muonium centers (Mu and Mu^*, respectively) observed in diamond[2], silicon[3,4], and germanium[5]. The most valuable information would be EPR results on hydrogen-containing centers except for the almost complete lack of such observations[6]. As a result, I will discuss selected EPR results on other centers, primarily in Si. Then I will combine features of these results with the current μSR data and suggest a physically plausible model for Mu and Mu^* which explains the data. Finally, I will return to experiments which have been done on H in Si and Ge and relate them to the proposed model.

The natural place to look for analogies to Mu and Mu^* is interstitial single donors. Lithium is such a donor but it immediately has a characteristic which is qualitatively different than found in the μ^+-containing centers; it is a shallow donor. The isolated Li donor in Si has a complicated EPR spectrum because of the inverted valley-orbit splitting[7]. It is also quite likely that an EPR spectrum of an isolated Li interstitial in Ge would be complicated because of the small valley-orbit splitting,[8] independent of whether it is inverted or not, although such a study has not been reported. Lithium is also known to associate with O in Si and Ge. In silicon an isotropic EPR spectrum typical of group V substitutional donors was observed for Li-O associates,[9] whereas in Ge[10] an anisotropic EPR spectrum similar to that for Sb was observed. The Sb spectrum[11] arises from the effects of strains in mixing the singlet and triplet valley-orbit split 1s ground states.[12] The resultant spectrum corresponds to the superposition of four spectra with axial

symmetry about the crystalline <111> axes such as is obtained for Mu^*. However, this similarity to the symmetry axes for Mu^* is fortuitous since strain mixing of the valley-orbit split 1s states for Si would produce <100> symmetry centers because of the different locations of the conduction band minima in Si and Ge.

Lithium provides us with no insight into the behavior of muonium-like centers since the hyperfine splitting of Mu is too large for it to be a shallow donor, and the Mu^* hyperfine interaction is too anisotropic to result from a shallow center unless strain coupling of the valley-orbit split levels occurs but then the symmetry may be wrong (also see the discussion of the anisotropy of the Mu^* hyperfine interaction below). In addition, theoretical studies[13] have suggested that interstitial H and μ^+ should produce deep donors because the pseudopotential is not reduced by core orbitals.

There are other interstitials which have been observed by EPR in silicon. The isolated Al^{++} interstitial[14] occupies the T_d interstice but the smaller B[15] and C^+[16] interstitials occupy distorted sites, presumably because of the Jahn-Teller effect[17]. The C^+ has orthorhombic symmetry and the B is monoclinic so no direct analogies to Mu^* result. Nonetheless it is interesting to note that these small interstitials are unstable in the tetrahedral interstice and spontaneously distort. In addition, we note that explanations of these centers using relatively simple molecular orbital arguments (linear combinations of atomic orbitals used to construct molecular orbitals - LCAO:MO) have been quite informative[1,14-16].

Deep substitutional donors have also been observed by EPR in semiconductors. Sulfur in silicon is a double donor and for the positve charge state, in which only one extra electron is bound to the sulfur, the EPR data[18] show that it has the full tetrahedral (T_d) symmetry of the substitutional site. However, N is a single deep donor in diamond[19] and silicon[20], rather than shallow like the other group V impurities, and it has axial symmetry about the <111> axes. The resultant molecular orbital is antibonding between Si and N and the electron spin density is largely on a single Si atom.[20] This, and the similar deep B[21] and F[22] donors in ZnO, are manifestations of the pseudo Jahn-Teller effect.[17]

I believe these are among the observations which will prove most useful in assessing the μSR data on Mu and Mu^* in group IV elemental semiconductors. In particular, we will find it useful to remember that small interstitials may distort, that deep substitutional donors distort along <111> axes because of the pseudo Jahn-Teller effect, and that LCAO:MO arguments have frequently been useful in analyzing deep centers in silicon.

With these EPR features as guides I wish to propose a moderately specific model of Mu and Mu^* which will be based on three features of the μSR data. First, the hyperfine parameter for Mu is about $\frac{1}{2}$ the vacuum value[2,4,5] (45% in Si to 83% in C). Second, for Mu^* $A_\parallel \approx \frac{1}{5} A_\perp$ and both are small.[2,3,5] Finally, conversion from Mu to Mu^* or the reverse is slow (rates < 0.1 μsec^{-1} for T < 100 K in Si).[23] In addition, I will make two reasonable simplifications, especially since there is no evidence nor physically plausible argument to suggest otherwise. The first is that impurities and other defects are not involved directly. The second is that the muon is not tunneling, i.e., the μSR observations result from the muon vibrating about a single equilibrium position for times > 10 μsec. We might regard the latter simplification somewhat more skeptically because the muon is so light. However, there is no μSR evidence of tunneling of the sort which can occur in EPR such as line broadening, unusual temperature dependence, complex spectra, or rapid relaxation. In addition, it would not appear that models involving impurities or tunneling agree with the observations as well as the one suggested below.

It will be helpful in our discussion of a model to analyze the hyperfine parameters obtained for Mu^*. In particular, we can analyze $A_\parallel$ and $A_\perp$ under the assumption that they arise only from s and p orbitals on the μ^+. Each makes a contribution to the hyperfine interaction. For axial symmetry we have[24]

$$A_\parallel = A_s + 2A_p,$$

$$A_\perp = A_s - A_p,$$

or

$$A_s = \frac{1}{3}(A_\parallel + 2A_\perp),$$

$$A_p = \frac{1}{3}(A_\parallel - A_\perp).$$

The result for A_s and A_p for diamond[2], silicon[23], and germanium[5] are given in the table along with the values for a 1s and a 2p orbital (the values are in MHz and correspond to 0 K or as low a temperature as data was available).

	C	Si	Ge	1s	2p
A_s	317.7	67.32	96.1	4463	0
A_p	-74.8	-25.27	-34.6	0	28

Table. Hyperfine parameters in MHz for Mu^* in various crystals and for a μ^+-centered 1s and 2p atomic orbital.

If the orbital wave function for Mu^* consists of a mixture of an s orbital and a p orbital directed along the symmetry axis, then A_s and A_p would have the same sign, in clear contradiction to the table. For axial symmetry, one cannot have the p orbital perpendicular to the symmetry axis unless the state is doubly degenerate. In that case, the center will be unstable to an asymmetric distortion (the Jahn-Teller effect[17]) and <111> axial symmetry would not be observed. In addition, we note that, since the p contribution could not exceed the value for a 2p atomic orbital, $|A_p|$ for Ge and diamond is larger than is possible. The value of A_s is also very small (7%, 1.5%, and 2% of that for a 1s orbital). Thus this superficial analysis fails to explain the Mu^* hyperfine parameters and also fails to account for the location of most of the electron spin density.

One of the earliest attempts at an explanation[3,25] of the nature of Mu and Mu^* suggests the direction a model might take. The suggestion was that Mu is a μ^+ in a T_d interstitial site and Mu^* is a μ^+ in a hexagonal site. If the electron spin is on the puckered hexagon of atoms which are nearest neighbors of the hexagonal interstitial site, the dipole-dipole interaction produces a value of A_p approximately equal to that observed for Si, including the correct sign. The sign agrees with simple classical argument for this model. The larger values of A_p for diamond and Ge may result from the smaller distance of part of the actual electron spin density from the muonium in the interstitial site. This feature of a hexagonal interstitial model for Mu^* was mentioned earlier.[3] As attractive as this may seem, it only explains A_p. Why is A_s so small and why, in view of the light mass and resultant large zero-point amplitude and vibrational frequency of the μ^+, does not all the muonium rapidly convert into the more stable form, Mu or Mu^*?

The model which I propose is simply a more detailed version of this model but it provides verifiable detail and a rationale for an otherwise primarily ad hoc model. Let us consider literally a simple LCAO:MO model in which atomic orbitals on the nearest neighbor (and next-nearest neighbor for T_d) Si atoms and the μ^+ are considered. The orbitals which will concern us are 1s (and possibly 2p) on μ^+ and 3s and 3p orbitals on Si, the valence orbitals. We will consider the standard sp^3 hybrids of the Si orbitals resulting in the four tetrahedrally directed orbitals used to discuss bonding. With overlap of these directed orbitals, one can talk about bonding and antibonding Si orbitals.

The Mu ground states is clearly about one-half 1s atomic orbital on the μ^+, and it is completely symmetric (Γ_1) in the T_d symmetry. Thus the molecular orbital will consist of some 1s orbital on the μ^+, and some of each of the two Γ_1 Si orbitals, one of which is bonding and one of which is antibonding. No other possibility exists for this simple LCAO:MO approach.

For Mu^* the symmetry of the ground state may be any of four possibilities for the D_{3d} symmetry. A completely symmetric (Γ_1^+) state is possible; consisting of an admixture of 1s orbital on the μ^+ and a Γ_1^+ Si bonding orbital on the puckered hexagon of nearest neighbor atoms. This is very analogous to the ground state in T_d symmetry. The only other possibility I will consider is a Γ_2^- orbital which consists of a Γ_2^- antibonding Si orbital and perhaps some 2p orbital on the μ^+. The antibonding orbital will be lowered in energy by an increase in the Si-Si spacing for the puckered hexagon surrounding the hexagonal interstitial site. The experimental data support the identification of the Γ_2^- orbital as the lower of the two. Symmetry prevents a 1s orbital admixture into a Γ_2^- function so there is a strong argument for the s orbital hyperfine interaction being so small (I suggest below how a small admixture can result). In addition, the stability of this orbital suggests a considerable displacement of the positions of the Si atoms in the puckered hexagon. The slow interconversion of Mu and Mu^* can then be seen to result from a failure of the Si vibrational functions to overlap rather than because of low muon vibrational overlap. The small admixture of 1s atomic orbital can be accounted for by mixing caused by the zero-point vibration of the muon which carries it out of the rotary-reflection plane of the D_{3d} symmetry.

It is often felt that a problem with the hexagonal interstitial model is its apparent disagreement with the conclusions of Picraux and Vook based on channeling studies of D in Si[26]. They concluded that D atoms implanted in crystalline Si do lie close to (but perhaps not exactly on) a <111> axis. The location they obtained was not the hexagonal interstitial site but one displaced by about 1.9 A from the hexagonal site. However, later work by Stein[27] on the infrared absorption, when combined with the channeling studies, suggests a picture in which the D(or H)is bound to a single silicon (attaches to a dangling bond) which is adjacent to a vacancy cluster. In brief, it is quite probable that the centers produced by stopping muons are different than any center in silicon observed so far involving hydrogen or its isotopes.

Another class of centers involving H which have been studied recently[28] in germanium are associates of hydrogen and another impurity, specifically C, Si, and O. These centers have been detected in very pure Ge by photothermal ionization spectroscopy. The hydrogen tunnels rapidly about the impurity and the center is a shallow donor in the case of O and a shallow acceptor if the impurity is C or Si. However, as mentioned earlier, shallow centers cannot explain the observed hyperfine parameter for either Mu or Mu^*, especially as similar centers are seen in all three elemental semiconductors. Thus again it appears that the observed hydrogen centers differ fundamentally from those involving muons.

In summary I have proposed a rather specific model for Mu and Mu^* in group IV semiconductors, a model which is physically plausible, has many features suggested by EPR studies of various centers in Si, fits the μSR data, and, perhaps most important, has what would appear to be verifiable characteristics. Observation of Si^{29} hyperfine interaction for six equivalent silicon sites, when combined with the existing data, would be strong confirmation of this model for Mu^*. In addition, DEMUR[29] experiments on Mu^* in Si and Ge would provide valuable information to compare to the model.

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REFFRENCES

1. G. W. Ludwig and H. H. Woodbury, in Solid State Physics, ed. F. Seitz and D. Turnbull (Academic Press, New York, 1962), Vol. 13, p. 223; G. D. Watkins in Radiation Damage in Semiconductors, ed. P. Baruch (Dunod, Paris, 1965), p. 97; J. W. Corbett, Electron Radiation Damage in Semiconductors and Metals (Academic Press, New York, 1966).
2. E. Holzschuh, W. Kündig, B. D. Patterson, H. Appel, J. P. F. Sellschop, and M. Stemmet, see paper entitled "Muonium in Diamond" in this issue.
3. B. D. Patterson, A. Hintermann, W. Kündig, P. F. Meier, F. Waldner, H. Graf, E. Recknagel, A Weidinger, and Th. Wichert, Phys. Rev. Lett. 40, 1347 (1978).
4. E. Holzschuh, W. Kündig, and B. D. Patterson, see paper entitled "Direct Measurement of the Hyperfine Frequency of Muonium in Silicon" in this issue.
5. E. Holzschuh, H. Graf, E Recknagel, A. Weidinger, Th. Wichert, and P. F. Meier, Phys. Rev. B 20, 4391 (1979).
6. The only report which I know about is: Y. V. Gorelkinskii, V. O. Sigle, and Z. S. Takibaev, Phys. Stat. Solidi A22, K55 (1974), who observe a shallow donor in hydrogen-implanted crystalline Si.

7. G. D. Watkins and F. S. Ham, Phys. Rev. B 1, 4071 (1970).
8. A. Adolf, D. Fortier, J. H. Albany, and K. Suzuki, Phys. Rev. Lett. 41, 1477 (1978).
9. G. Feher, Phys. Rev. 114, 1219 (1959); R. L. Aggarwal, P. Fisher, V. Mourzine, and A. K. Ramdas, Phys. Rev. 138. A882 (1965).
10. E. E. Haller and L. M. Falicov, Phys. Rev. Lett. 41, 1192 (1978).
11. R. E. Pontinen and T. M. Sanders, Jr., Phys. Rev. 152, 850 (1966).
12. D. K. Wilson, Phys. Rev. 134, A265 (1964).
13. M. Altarelli and W. Y. Hsu, Phys. Rev. Lett. 43, 1346 (1979); L. Resca and R. Resta, Solid State Comm. 29, 275 (1979); L. Resca and R. Resta, Phys. Rev. Lett. 44, 1340 (1980).
14. K. L. Brower, Phys. Rev. B 1, 1908 (1970).
15. G. D. Watkins, Phys. Rev. B 12, 5824 (1975).
16. G.D. Watkins and K. L. Brower, Phys. Rev. Lett. 36, 1329 (1976).
17. M. D. Sturge, in Solid State Physics, ed. F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press, New York, 1967), Vol 20, pg. 91; F. S. Ham, in Electron Paramagnetic Resonance, ed. S. Geschwind (Plenum, New York, 1972), pg. 1; R. Englman, The Jahn-Teller Effect in Molecules and Crystals (J. Wiley, New York, 1972); T. L. Estle, in Optical Properties of Ions in Solids, ed. B. DiBartolo (Plenum, New York, 1975), pg. 419.
18. G. W. Ludwig, Phys. Rev. 137, A1520 (1965).
19. W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, Phys.Rev. 115, 1546 (1959); J. H. N. Loubser and L. du Preez, Brit. J. Appl. Phys. 16, 457 (1965).
20. K. L. Brower, Phys. Rev. Lett. 44, 1627 (1980).
21. A. R. Reinberg, J. Chem. Phys. 41, 850 (1964).
22. A. R. Reinberg and T. L. Estle, Phys. Rev. 160, 263 (1967).
23. K. W. Blazey, J. A. Brown, D. W. Cooke, S. A. Dodds, T. L. Estle, R. H. Heffner, M. Leon, and D. A. Vanderwater, see paper entitled "Temperature Dependence of Anomalous Muonium Hyperfine Interaction in Silicon" in this issue.
24. A. N. Jette, Phys. Rev. 184,604 (1969).
25. Yu. M. Belousov, V. N. Gorelkin, and V. P. Smilga, Sov. Phys. JETP 47, 331 (1978); Yu. M.Belousov, V. N. Gorelkin, and V. P. Smilga, Sov. Phys. JETP 48, 1007 (1978).
26. S. T. Picraux and F. L. Vook, Phys. Rev. B 18, 2066 (1978).
27. H. J. Stein, Phys. Rev. Lett. 43, 1030 (1979).
28. E. E. Haller, B. Jodo, and L. M. Falicov, Phys. Rev. B 21, 4729 (1980); B. Jodo, E. E. Haller, and L. M. Falicov, to appear in Phys. Rev. B.

29. J. A. Brown, R. H. Heffner, M. Leon, S. A. Dodds, D. A. Vanderwater, and T. L. Estle, Phys. Rev. Lett. 43, 1751 (1979); D. A. Vanderwater, J. A. Brown, D. W. Cooke, S. A. Dodds, T. L. Estle, R. H. Heffner, and M. Leon, see paper entitled "DEMUR: Double Electron Muon Resonance" in this issue.