theory was nowhere adjusted to agree with the specific-heat data. Consequently, from the small and fluctuating $\lambda^{SF} = \lambda^{tot} - \lambda^{ep}$ for $0.8 \geq c_{Pd}$, we conclude that there are no paramagnons in these alloys. Since the electron-phonon interaction is still quite large for $c_{Pd} = 0.8$ and 0.7 we can thus expect superconductivity. For orientation we note that for $\lambda_{eff} = \lambda^{tot} = 0.43$, $\omega_{log} = 130$ K, and $\mu^* = 0.13$, we obtain[12] $T_c = 0.49$ K. Even if we take $\lambda^{tot} - \lambda^{ep} = \lambda^{SF}$ and therefore $\lambda_{eff} = \lambda^{ep} - \lambda^{SF}$ we get $T_c = 50$ mK.

Up till now we made no use of any model for the paramagnetic fluctuations. In order to ascertain whether the above picture is consistent with such models we calculated λ^{SF} from a simple one-parameter theory[18] which give $\lambda^{SF} = \frac{9}{2} \ln(S/3)$ where S is the Stoner enhancement factor $S = [1 - In(\epsilon_F)]^{-1}$. For $I = 0.787$ which gives $S = 10$ for pure Pd, the values of λ^{SF} for the first three of our alloys is shown in Fig. 2 and Table I. As is well known, such a simple model cannot fit both the specific heat data and the susceptibility. Nevertheless, λ^{SF} calculated above clearly indicates that one should not expect much λ^{SF} beyond $c_{Pd} = 0.8$. Note that the steep fall of S in the above calculation is consistent with the observed decrease of the susceptibility[6] χ.

In conclusion we note that if the alloys Pd_cAg_{1-c} with $0.8 \geq c_{Pd} \geq 0.6$ do indeed turn out to be superconductors they will be a most interesting class of systems in which one can study the interaction between magnetic fluctuations and superconductivity. Moreover, such an observation would be a strong hint that the superconductivity in amorphous Pd is merely a sign of the absence of paramagnons due to reduction in $n(\epsilon_F)$ by disorder.

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Why Muons and Protons are Deep Donors in Si and Ge

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The deep impurity character of interstitial positive muons or protons in Si and Ge is shown to result from the valley-orbit interaction of the six conduction-band minima along Δ. This interaction, much stronger for interstitial than for substitutional point charges, leads to a breakdown of the effective-mass approximation and to the formation of a deep state. This is particularly striking in Ge, where the Δ minima are not the absolute ones.

Positive muons, injected into Si or Ge crystals, can capture an electron and form an impurity state analogous to muonium, after they come to rest in an interstitial position.[1] Although the binding energy is not measured directly, hyperfine frequency measurements show that the electron probability density at the muon is reduced, with respect to a free muonium, by a factor of

about 0.5 only (0.56 for Ge,[2] 0.45 for Si[3]), suggesting a very tightly bound state. The same conclusion might apply to interstitial protons as well, since no effect of hydrogen impurities on the electrical properties of Si and Ge has ever been detected.

From the theoretical point of view, the deep binding of electrons to these point-charge impurities is surprising, in view of the well-known effective-mass arguments leading to the correct prediction of a binding energy of a few tens of meV to impurities such as P in Si or As in Ge, which correspond to adding a point charge (a proton) at a lattice site. Since in the traditional effective-mass approach[4] no reference is made to the position of the impurity in the unit cell, a similar binding energy would be expected for an interstitial position of the point charge. Earlier attempts to resolve the paradox[5-7] were based on *ad hoc* formulations that lack any rigorous justifications.[8]

It has recently been pointed out by many authors[9-11] that the effective-mass theory of impurity states must be drastically modified for semiconductors with a multivalley band structure. The resulting equations imply a strong dependence of the binding energy not only on the impurity potential, but also on the position of the impurity in the unit cell,[12] and the possibility of a deep ground state as a result of the valley-orbit interaction.[13] The purpose of the present work is to show that this interaction is indeed strongly site dependent and that it explains why interstitial point charges act as deep donor impurities in Si, while the same point-charge impurity potential on a lattice site produces shallow levels. An extension of the same ideas to Ge shows that, via the same mechanism, the contribution to interstitial impurity states of the six Δ minima, that are ~ 0.1 eV above the absolute L minima, triggers the formation of a state much deeper than the states derived from the L valleys only. This is the first demonstration that the role of higher critical points in the band structure can be so dramatic as to change the character of an impurity from shallow to deep.

We start by recalling that in multivalley semiconductors the impurity potential U mixes Bloch functions $|\vec{k}\rangle$ and $|\vec{k}'\rangle$ belonging to different valleys, and that the corresponding matrix element can be written

$$\langle\vec{k}|U|\vec{k}'\rangle=\sum_{\vec{G}}c(\vec{k},\vec{k}';\vec{G})\tilde{U}(\vec{k}-\vec{k}'-\vec{G}), \qquad (1)$$

where $\vec{G}$ are the reciprocal-lattice vectors, $c(\vec{k},\vec{k}';\vec{G})$ are Fourier coefficients of the product of periodic parts of $|\vec{k}\rangle$ and $|\vec{k}'\rangle$, and $\tilde{U}$ is the Fourier transform of $U(\vec{r})$. It has been shown[9-11] that the replacement of Bloch functions with simple plane waves, as done in the usual effective-mass treatments, leads to gross errors in the evaluation of Eq. (1) and that a large number of "umklapp" vectors $\vec{G}$ contribute to the summation. A change in the position of the impurity by a vector $\vec{\tau}$, which affects each term of Eq. (1) by a factor $\exp(i\vec{G}\cdot\vec{\tau})$, can then lead to a large modification of its value.[12]

We shall characterize the strength of the intervalley interaction between valleys i and j by introducing a dimensionless renormalization factor λ_{ij}, which is defined by

$$\langle\vec{k}_{oi}|U|\vec{k}_{oj}\rangle=\lambda_{ij}4\pi e^2/\epsilon(\vec{k}_{oi}-\vec{k}_{oj})|\vec{k}_{oi}-\vec{k}_{oj}|^2 \qquad (2)$$

i.e., it is the ratio of the matrix element between wave functions at the bottom of the valleys to the Fourier transform of a screened Coulomb potential which would result from a standard effective-mass treatment.

As shown in Refs. 9 and 11, for substitutional point-charge impurities in Si, the factors λ are of the order of 0.3–0.4 (and even smaller if the short-range part of the Coulomb potential is replaced by a weaker pseudopotential).[14] These values, much smaller than 1, determine the shallow nature of substitutional donors in Si, because, as emphasized by Herbert and Inkson,[13] a deep level is obtained in Si whenever the renormalization factor is close to 1 or larger. We have performed pseudopotential calculations of intervalley matrix elements for a screened point-charge potential at the high-symmetry tetrahedral and hexagonal interstitial sites of Si, using the form factors of Chelikowsky and Cohen[15] with a basis set of 88 plane waves, and the diagonal dielectric function of Vinsome and Richardson.[16] The results are shown in Table I, where the contribution of each shell to Eqs. (1) and (2) is shown separately, and where the results of Ref. 11 for the substitutional case are shown for comparison. The valley-orbit interaction is much stronger at interstitial sites, thus explaining the deep-donor character of interstitial muons (and protons) in Si in terms of the microscopic variations of the Bloch functions inside the unit cell.

It is natural to ask, in view of the total analogy of experimental results, whether the same theoretical arguments carry over to Ge. In Ge, the four minima at L are characterized by very light effective masses that, together with the larger

TABLE I. Contribution of individual G shells and total value of the renormalization factors for a substitutional or interstitial screened point-charge impurity potential in Si. For substitutional or tetrahedral interstitials, there are 2 inequivalent classes of valley pairs, while there are 3 for the hexagonal site, as indicated at the top of each column. k_0 is 0.86 in units of $2\pi/a$.

	G shell									
Interstitial	⟨000⟩	⟨111⟩	⟨200⟩	⟨220⟩	⟨311⟩	⟨222⟩	⟨400⟩	⟨331⟩	⟨420⟩	⟨422⟩	Total
Substitutional											
$(k_0,0,0)$, $(\bar{k}_0,0,0)$	−0.198	−1.066	0.000	0.955	0.360	0.000	0.001	0.244	0.000	0.006	0.30
$(k_0,0,0)$, $(0,k_0,0)$	0.397	−0.519	0.000	0.324	0.092	0.000	0.001	0.076	0.000	0.003	0.38
Tetrahedral											
$(k_0,0,0)$, $(\bar{k}_0,0,0)$	−0.198	1.066	0.000	0.955	−0.360	0.000	0.001	−0.244	0.000	0.006	1.23
$(k_0,0,0)$, $(0,k_0,0)$	0.397	0.519	0.000	0.324	−0.092	0.000	0.001	−0.076	0.000	0.003	1.08
Hexogonal											
$(k_0,0,0)$, $(\bar{k}_0,0,0)$	−0.198	0.754	−0.001	0.000	0.254	0.296	−0.001	−0.172	0.000	0.000	0.93
$(k_0,0,0)$, $(0,k_0,0)$	0.397	0.581	−0.252	0.283	0.071	0.091	−0.009	−0.065	0.010	−0.005	1.10
$(k_0,0,0)$, $(0,\bar{k}_0,0)$	0.397	0.153	0.252	−0.283	0.058	0.091	−0.009	−0.043	−0.010	0.005	0.61

dielectric constant, give rise to very shallow levels for substitutional point-charge donors, even though the intervalley renormalization factor[11] is 2.3. It turns out that at interstitial sites the corresponding factor is severely reduced, to a value of about 0.7. An interstitial muonium state derived only from L wave functions would therefore be more shallow than substitutional-donor levels, with a binding energy of the order of 10 meV.

It is, however, important to observe that a set of six Δ minima, quite analogous to those of Si, exists in Ge, and their energy, according to pseudopotential calculations,[17] is only ~0.1 eV higher than the L minima. Should a strong intervalley interaction exist between these minima, its strength could easily compensate for their higher energy, and produce a state much more tightly bound that its L counterpart. Table II shows indeed that this cannot be the case for substitutional point-charge impurities, where the renormalization factors (for the Δ valleys) are much smaller than 1, but certainly happens for interstitials, where these factors exceed 1.[18] Since effective masses at Δ are very similar to those of Si (we estimate $m_{\parallel}=0.9m_0$ and $m_{\perp}=0.2m_0$ from pseudopotential calculations), such a large valley-orbit interaction results in a deep ground state for muonium in Ge as well. It is understood that when a deep state is formed, the whole Brillouin zone contributes to it. However, we can identify the valley-orbit interaction of the Δ minima as the driving force for the localization of the state.

This result for Ge is a striking example for the effects that subsidiary extrema of the band structure can have on impurity states.[19] It also suggests that these extrema can alter the shallow or deep character of an impurity.

It is important to emphasize that the deep nature of the ground state of muonium in Si is a consequence of the interstitial position of the muon and of the strong short-range behavior of the Coulomb potential. When either of these two

TABLE II. Same as Table I for substitutional and tetrahedral interstitial impurities in Ge. k_0 is 0.84 in units of $2\pi/a$.

	G shell									
Interstitial	⟨000⟩	⟨111⟩	⟨200⟩	⟨220⟩	⟨311⟩	⟨222⟩	⟨400⟩	⟨331⟩	⟨420⟩	⟨422⟩	Total
Substitutional											
$(k_0,0,0)$, $(\bar{k}_0,0,0)$	-0.109	-1.157	0.000	0.814	0.320	0.000	0.069	0.235	0.000	0.062	0.23
$(k_0,0,0)$, $(0,k_0,0)$	0.441	-0.560	0.000	0.341	0.093	0.000	0.023	0.073	0.000	0.022	0.43
Tetrahedral											
$(k_0,0,0)$, $(\bar{k}_0,0,0)$	-0.109	1.157	0.000	0.814	-0.320	0.000	0.069	-0.235	0.000	0.062	1.44
$(k_0,0,0)$, $(0,k_0,0)$	0.441	0.560	0.000	0.341	-0.093	0.000	0.023	-0.073	0.000	0.022	1.22

causes is absent, a shallow ground state occurs. Indeed, Li interstitials are experimentally known to produce shallow bound states.[20] This is because in the Li^+ pseudopotential, orthogonality to the two core electrons has a repulsive effect on s states, which largely cancels the Coulomb potential at short distances. This effect is accounted for empirically in the nonlocal model potential of Animalu and Heine.[21] We have performed a calculation for Li in Si, by screening this bare s-wave potential with the Si dielectric function,[16] and computing the λ factors obtained when the resulting potential is located at the tetrahedral interstitial position. All momentum components are severely reduced with respect to the Coulomb case, and λ_{ij} is practically vanishing for i and j on the same Δ axis, and equals 0.365 for i and j on different Δ axes. The resulting binding energy of the A_1 level, as computed by the methods of Ref. 11, is about 45 meV, in semiquantitative agreement with the experimental value of 31 meV.[20] While a more quantitative analysis undoubtedly requires a better and more consistent description of the Li potential in a Si host, it is nonetheless gratifying to recover a shallow bound state when the effect of the core electrons is crudely accounted for.

In conclusion, it was shown that the puzzling deep-donor character of interstitial point charges in Si and Ge is explained by the strong valley-orbit interactions of the six Δ valleys, and the first direct evidence of the shallow-deep instability mechanism discussed by Herbert and Inkson[13] was provided. The results also prove that the role of higher critical points of the band structure can be crucial for impurity states, and confirm that a correct evaluation of intervalley interactions is of great importance in the description of donor states in Si and Ge.

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