treatment of the spin-wave theory, taking into account anharmonic effects, be done with the sufficient rigor that its accuracy could be assessed at the temperatures and fields of the experiment. A subtraction could then be done to determine the amplitude of the nonperturbative effects. We expect that the contribution of breather modes, which are essentially bound pairs of spin waves, would be included in the perturbation theory, and would not make any separate contribution to the intensities, although they might produce observable effects in the shape of the spectrum. The nonperturbative contribution to the total intensity could presumably be associated with the solitons, and may be describable by (8). Inasmuch as no such separation has been accomplished to date, one cannot say that solitons have been observed in $CsNiF_3$.

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Substitutional Donors and Core Excitons in Many-Valley Semiconductors

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The shallow-deep instability of substitutional donors and core excitons is discussed, with inclusion of all intervalley interactions. Shallow levels result in Si for a screened point-charge potential, because intervalley overlap and kinetic energy balance the potential-energy terms, which are severely reduced, at substitutional sites, by umklapp effects. Contrary to recent claims based on consideration of potential energy only, many-valley interactions cannot therefore be invoked to predict deep core-exciton levels in Si.

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Much interest in impurity states in semiconductors with many-valley bands has recently been stimulated by the experimental discovery that interstitial muonium is a deep donor in Si and Ge,[1] by suggestions that core-exciton levels may also be deep,[2] and by the theoretical discovery that drastic modifications of the traditional[3] effective-mass approach are needed to account for intervalley interactions properly.[4-7] In the theoretical description of muonium in Si and Ge,[8,9] two effects have been considered to explain its deep-level character. One is the point-charge nature of the muon potential, as contrasted with weaker pseudopotentials for impurity atoms with core electrons; the other is the location of the muon at the interstitial site, where intervalley matrix elements of the point-charge potential are ~3–4 times larger than at the substitutional site.[9] Very recently,[10] it has been argued that the second effect (the site dependence) plays no role and that, in fact, deep levels result in Si from a screened point-charge potential, irrespective of its location. In view of the relevance of the question in general, and in particular for the problem of core excitons, which can be described as electrons bound by the nearly pointlike charge of a core hole in a host atom, the purpose of the present Letter is to discuss the energy levels of a

substitutional point-charge (pseudo)potential in Si. It will be shown explicitly that when all intervalley interactions are included, shallow levels are obtained, and that deep levels arise only when, as in Ref. 10, intervalley overlap and kinetic-energy interactions are ignored.

The crucial role of such terms in determining the shallow versus deep nature of donor levels in many-valley semiconductors is clearly pointed out in the lucid discussion of Herbert and Inkson,[7] based on the $\vec{k}$-space formulation of the problem, also adopted in Refs. 6 and 9. If we denote by $H = H_0 + V$ the Hamiltonian of the perturbed crystal, where H_0 is the perfect-crystal Hamiltonian and V the screened point-charge potential, its eigenfunctions of a given symmetry are written in terms of Bloch functions ψ_c as

$$\varphi = \sum_i \alpha_i \int d^3k\, c(\vec{k} - \vec{k}_{0i})\psi_c(\vec{k}, \vec{r}) \equiv \sum_i \alpha_i \varphi_i , \tag{1}$$

where i labels the conduction-band valleys centered at $\vec{k}_{0i}$, c is an envelope function centered around the valley minimum, and the α_i are numerical coefficients determined by group-theoretical methods. Applying the variational principle to Eq. (1), one finds

$$E = \min \frac{\sum_{i,j} \alpha_i^* \alpha_j (\langle \varphi_i | H_0 | \varphi_j \rangle + \langle \varphi_i | V | \varphi_j \rangle)}{\sum_{i,j} \alpha_i^* \alpha_j \langle \varphi_i | \varphi_j \rangle} . \tag{2}$$

The terms with $i \neq j$ in the first term of the numerator and in the denominator are, respectively, the intervalley kinetic-energy and overlap terms. They arise because the one-valley functions $c(\vec{k} - \vec{k}_{0i})$ have tails that "spill" into the other valleys; in fact, it should be kept in mind that a function with *exponential* localization in r space, $\sim e^{-\gamma r}$, corresponds to a function with *algebraic* localization in k space, $\sim (\gamma^2 + k^2)^{-2}$. If such terms, which grow very rapidly as the trial function spreads out in $\vec{k}$ space, are neglected, a deep s-like (Γ_1) level is indeed obtained in Si for a substitutional point-charge impurity. This is shown in Table I, where I list the binding energy computed with the methods of Refs. 6 and 9, and where, to facilitate comparison with the results of Resca and Resta,[10] we assumed isotropic valleys with $m^* = 0.2987 m_0$. While full consideration of Eq. (2) gives a 64 meV binding energy, omission of the intervalley kinetic-energy terms produces a deep level with ~ 1-eV binding, and omission of both kinetic and overlap terms further deepens the level to ~ 1.7 eV. The numerical values of these deep energies are, of course, meaningless, but they are shown to demonstrate the dramatic effect of kinetic and overlap terms in balancing the attractive intervalley potential energy. This is also apparent from the breakdown of the binding energy into the expectation values of intravalley and intervalley kinetic and potential energies. It is interesting to observe that the intravalley overlap accounts for 98% of the normalization and that intervalley overlap only accounts for 2%, so that the envelope functions are quite localized in the respective valleys, but nonetheless the intervalley kinetic energy is quite large, because of the parabolic rise of $E(\vec{k})$ within each valley.

It is now easy to see that the kinetic and overlap terms are completely neglected in the approach of Resca and Resta,[8,10] which consists of rewriting Eq. (1) in the form

$$\varphi = \int d^3\eta\, c(\vec{\eta}) \sum_i \alpha_i \psi_c(\vec{k}_{0i} + \vec{\eta}, \vec{r}) \equiv \int d^3\eta\, c(\vec{\eta}) |\vec{\eta}\rangle , \tag{3}$$

and in the assumptions that the symmetrized combinations of Bloch functions $|\vec{\eta}\rangle$ form a set of functions which[8] (a) is orthonormal and (b) diago-

TABLE I. $E_B(a)$: Ground-state energy for the substitutional screened point-charge impurity potential in Si, computed when isotropic valleys with $m^* = 0.2987\ m_0$ are assumed. The value in parentheses is the corresponding result for the interstitial site. T_{intra}, V_{intra}, T_{inter}, and V_{inter} are the expectation values of intravalley kinetic, intravalley potential, intervalley kinetic, and intervalley potential energies, respectively, in the ground state. O_{intra} and O_{inter} are the contributions of the $i = j$ and $i \neq j$ terms, respectively, to the norm of the state, $\Sigma_{ij} \alpha_i^* \times \alpha_j \langle \varphi_i | \varphi_j \rangle$ (see text). $E_B(b)$: Same as $E_B(a)$, but computed with neglect of intervalley kinetic-energy terms in Eq. (3). $E_B(c)$: Same as $E_B(b)$, but with neglect also of intervalley overlap terms. All energies are in millielectronvolts.

$E_B(a)$	T_{intra}	V_{intra}	T_{inter}	V_{inter}	O_{intra}	O_{inter}	$E_B(b)$	$E_B(c)$
−64.1 (−3349.5)	239.5	−206.3	45.8	−143.0	0.9797	0.0202	−1000.4	−1753.7

nalizes H_0. It is quite easy to see that, instead,

$$\langle\vec{\eta}|\vec{\eta}'\rangle = \delta(\vec{\eta}-\vec{\eta}') + \sum_{i,j}{}' \alpha_i^* \alpha_j \delta((\vec{k}_{0i}-\vec{k}_{0j})-(\vec{\eta}'-\vec{\eta})), \tag{4}$$

and that

$$\langle\vec{\eta}|H_0|\vec{\eta}'\rangle = (\eta^2/2m^*)\delta(\vec{\eta}-\vec{\eta}') + \sum_{i,j}{}' \alpha_i^* \alpha_j E(\vec{k}_{0j}+\vec{\eta}')\delta((\vec{k}_{0i}-\vec{k}_{0j})-(\vec{\eta}'-\vec{\eta})), \tag{5}$$

where the prime indicates that summations are restricted to $i \neq j$. The additional terms are present for $\vec{\eta}$'s comparable to intervalley vectors, which necessarily appear in the "tail" of $c(\vec{\eta})$. Using Eqs. (4) and (5), one finds for $F(\vec{r})$, the Fourier transform of $c(\vec{\eta})$, the Schrödinger equation obtained in Ref. 8, but with an additional complicated repulsive, energy-dependent and nonlocal operator, which embodies intervalley kinetic and overlap corrections. It is the neglect of this operator, and *not a better treatment of the potential energy terms*, that leads to the prediction of a deep substitutional level in Refs. 8 and 10.

In the process of comparing $\vec{k}$-space and $\vec{r}$-space approaches to the many-valley impurity problem, it is also interesting to clarify how the difference in potential-energy intervalley matrix elements is reflected in the two approaches. In the $\vec{r}$-space approach,[8] the intervalley effect is contained in a renormalization factor $|\rho(0,\vec{r})|^2$ which multiplies the impurity potential $V(\vec{r})$,

$$V_{\text{eff}}(\vec{r}) = |\rho(0,\vec{r})|^2 V(\vec{r}), \tag{6}$$

and which is the charge density associated with the symmetrical combination of valley-bottom Bloch functions, $|\vec{\eta}=0\rangle$. In Fig. 1, I show the spherical average of $|\rho(0,\vec{r})|^2$ multiplied by the volume-element factor $4\pi r^2$, for Bloch waves symmetrized about the substitutional or the tetrahedral site. Apart from the r^2 factor, this is therefore the same quantity shown in Fig. 1 of Ref. 10 (except that I took the fully converged results obtained from an expansion of the pseudo Bloch functions in 89 plane waves). This figure shows that the charge of the six interfering Bloch waves, located within a radius of ~ 4 a.u. from the origin, is about 3.5 times bigger in the interstitial case than in the substitutional case. Since this region corresponds to the deep part of the potential, where dielectric screening is reduced from its long-wavelength value, it is little wonder that this results in intervalley (i.e., large momentum transfer) matrix elements about 3.5 times bigger in the interstitial than in the substitutional site, as found indeed by explicit calculations.[9,11] The charge localized in the above-mentioned region is the important quantity to compare, rather than the values of $|\rho(0,\vec{r})|^2$ at $\vec{r}$ exactly equal to zero,[10] which has zero weight in any matrix-element or radial-wave-equation calculation. This confirms, with support from both $\vec{r}$-space and $\vec{k}$-space calculations, the important role of site-dependent effects in determining the deep or shallow character of point-charge impurity levels in Si.

In conclusion, the present understanding of the shallow-deep instability in Si can be summarized as follows:

(a) Intervalley effects cannot be invoked to predict deep core-exciton levels in Si. The intervalley potential energy is not strong enough to overcome the kinetic and overlap effects. (Valence excitons are also shallow, because, needless to say, they have *no intervalley mixing*.)

(b) The potential-energy terms are strong

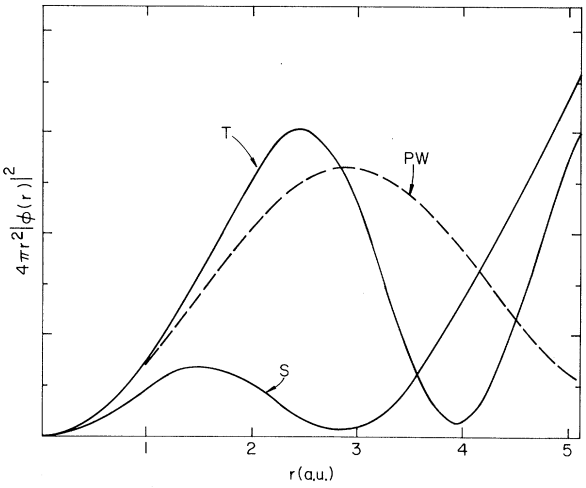

FIG. 1. Angle-integrated radial charge density (arbitrary units) of a superposition of the six valley-bottom Bloch pseudowave functions of Si, with full (Γ_1) tetrahedral symmetry with respect to the origin, which is at a substitutional site (S), or at a tetrahedral interstitial site (T). The curve labeled PW, also shown for reference, results from approximating the Bloch functions with single plane waves and is independent of the origin.

enough to give a deep level at the interstitial site for point-charge impurities, however, and account for the deep character of muonium states. The point-charge nature of the potential is also crucial, besides the site dependence, because, e.g., Li is a shallow interstitial, as shown by experiment[12] and theory.[13]

(c) Since the point-charge model appears to be an upper limit of short-range strength for group-V donors in Si (with the exception[14] of the strongly electronegative N) the present theory recovers, of course, the experimentally well-known shallow nature of P, As, Sb, and Bi donors.

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