The principal conclusions are that the induced magnetization density in metallic Sc is not like that of a single $3d$ electron in atomic Sc, and that the APW calculation of Gupta and Freeman gives quite good agreement with our results. From the temperature dependence of the susceptibility, Spedding and Croat[8] have inferred that Sc behaves as though there were a single localized $3d$ electron. Our results seem inconsistent with this interpretation.

The first exploratory measurements on this problem were carried out while one of us (W.C.K.) was a guest scientist at the Brookhaven National Laboratory. This author wishes to acknowledge with thanks the hospitality extended to him by the entire staff of BNL generally and by Dr. Gen Shirane and Dr. David Cox in particular. We wish to thank Mr. J. L. Sellers of Oak Ridge National Laboratory for valuable technical assistance.

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Indirect Exciton Dispersion and Line Shape in Ge

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The effective-mass equation for indirect excitons in Ge is solved taking the degeneracy and anisotropy of the bands into account. The calculated binding energies of the anisotropy split ground state (4.18 and 3.17 meV) are in excellent agreement with experiment (4.15 and 3.14 meV). The method is then extended to calculate the energy-momentum dispersion of excitons, which are strongly nonparabolic, and account well, with no adjustable parameters, for the recently measured modulated absorption line shape.

The interest in the indirect exciton spectrum of Ge has recently been stimulated by the accurate wavelength-derivative transmission spectra of Frova *et al.*[1] This experiment has determined that the exciton ground state is split by the conduction-band-valley anisotropy into two levels separated by 1.01 ± 0.03 meV, and that the energy–translational-momentum dispersion relations of the two exciton branches are strongly nonparabolic, and display the "mass-reversal" effect predicted by Kane.[1,2]

From the theoretical point of view, the solution of the effective-mass equation for indirect excitons in cubic semiconductors is difficult be-cause, while the anisotropy of the conduction-band valleys is too large to be dealt with in perturbation theory, the degeneracy of the valence bands makes the variational problem rather complicated, thus forcing the use of simple trial functions with few parameters. Recently[3] the authors have shown that this problem can be conveniently treated in a tensor-operator formalism which fully exploits the symmetry of the Hamiltonian and the powerful apparatus of angular momentum theory. It was shown[3] in particular that the indirect excitons of Ge are well described by an "axial model" in which the valence bands are assumed to have axial symmetry about the $\langle 111\rangle$ axis of the conduction-band ellipsoid.

The purpose of the present Letter is twofold: (a) to show that calculations based on this model yield theoretical binding energies of indirect excitons in Ge in excellent agreement with experiment, and (b) to show that this method can be extended to calculate the exciton energy-momentum dispersion relations. We thus obtain, for the first time, accurate values of the translational exciton masses in Ge, confirming quantitatively the mass-reversal effect predicted by Kane,[1,2] and obtaining a theoretical density of states which, without adjustable parameters, accounts quantitatively for the optical line shape reported in Ref. (1).

We start by writing the axial-model effective-mass Hamiltonian for indirect excitons in Ge,[3] in reduced units:

$$\begin{aligned} H_{\mathrm{ex}} &= H_e(\vec{\mathrm{p}}) - H_h(\vec{\mathrm{p}}) - 2/r \\ &= p^2 - 2/r - \tfrac{1}{9}\mu\,(P^{(2)}\cdot J^{(2)}) - \tfrac{2}{9}(\sqrt{70}/5)\,\delta[P^{(2)}\cdot J^{(2)}]_0^{\,4} - (\tfrac{2}{3})^{1/2}(\mu_0/\mu_{1e})P_0^{\,(2)}, \end{aligned} \tag{1}$$

where, in terms of the Luttinger parameters γ_1, γ_2, γ_3 and of the longitudinal and transverse electron masses, $m_{e\parallel}$ and $m_{e\perp}$,

$$\begin{aligned} \mu_0 &= \tfrac{1}{3}(2/m_{e\perp} + 1/m_{e\parallel}), \\ \mu_{1e} &= \tfrac{1}{3}(1/m_{e\perp} - 1/m_{e\parallel}), \\ \mu &= \mu_0(6\gamma_3 + 4\gamma_2)/5, \\ \delta &= \mu_0(\gamma_3 - \gamma_2). \end{aligned} \tag{2}$$

The irreducible spherical tensor operators of rank 2, $P^{(2)}$ and $J^{(2)}$, were defined in Ref. 4 and the physical meaning of the various terms was discussed in Ref. (3). In order to solve the Schrödinger equation corresponding to the Hamiltonian Eq. (1), we expand the wave function in the $\vec{\mathrm{F}}$, F_z representation, where $\vec{\mathrm{F}} = \vec{\mathrm{L}} + \vec{\mathrm{J}}$, i.e., the sum of the "orbital" angular momentum of the evelope function, with the spin $\frac{3}{2}$ corresponding to the valence-band degeneracy.[4] In Ref. (3) it was shown that inclusion of terms up to $L = 2$ in the expansion resulted in binding energies of 3.14 and 3.94 meV, respectively, for the $F_z = \pm\frac{1}{2}$ and the $F_z = \pm\frac{3}{2}$ components of the ground-state doublet.

The experimental values,[1,5] however, are 3.14 and 4.15 meV, respectively, so that while the agreement is very good for the shallower exciton, it is not as satisfactory for the deeper one. A possible cause for the disagreement could be the admixture of $L = 4$, or g-like, components in the wave functions, induced by the term in δ in H_{ex}. We have therefore extended our expansion to include states with $L = 4$; for the 1s and 2s exciton doublets, the results are shown in Table I. It is important to notice that we find excellent agreement with the experimental data, and in particular with the splitting[1] of the 1s doublet, which is known more accurately than the absolute binding energies.

We now turn our attention to the problem of the exciton dispersion. If the exciton translational momentum, $\vec{\mathrm{K}}$, is different from the location of

TABLE I. Theoretical (T) and experimental (E) values of the binding energies of 1s and 2s exciton states of Ge (in meV). In the last column the absolute square of the theoretical envelope function at the origin, $|F(0)|^2$, which determines the oscillator strength of the exciton state, is given.

Exciton state	Binding energy (T)	Binding energy (E)	$\lvert F(0)\rvert^2(T)$
1s $F_z = \pm\frac{3}{2}$	4.18	4.15	18.46
$F_z = \pm\frac{1}{2}$	3.17	3.14	7.31
2s $F_z = \pm\frac{3}{2}$	1.32	...	2.32
$F_z = \pm\frac{1}{2}$	0.87	...	0.85

TABLE II. Dispersion parameters (see text).

E_s (meV)	E_d (meV)	r_{ls}	r_{ld}	r_{ts}	r_{td}	r_{tc}	r_{mc}
−3.675	0.505	0.836	0.123	3.288	−0.820	1.669	0.8

the conduction-band minimum, $\vec{K}_0$, the effective-mass Hamiltonian, Eq. (1), is modified[6] and becomes

$$H_{\text{ex}} = H_e(\vec{p}+\tfrac{1}{2}\vec{k}) - H_h(\vec{p}-\tfrac{1}{2}\vec{k}) - 2/r, \tag{3}$$

where $\vec{k}=\vec{K}-\vec{K}_0$. Since H_e and H_h are quadratic forms in their arguments, new terms arise which are either quadratic in the $\vec{k}$ components or bilinear in the $\vec{k}$ and $\vec{p}$ components. The expression of the Hamiltonian Eq. (3) in terms of spherical tensor operators is rather lengthy, and will be given elsewhere.[7] Here we wish to remark only that, within the axial model, the eigenvalues of Eq. (3) will depend only on k_l and k_t, the components of $\vec{k}$, respectively parallel and perpendicular to the ⟨111⟩ direction, and not on the orientation of k_t in its plane. Furthermore, when $k_t=0$, i.e., for $\vec{k}$ in the Λ direction, F_z is a good quantum number, and the two components of the exciton are not mixed. When $k_t \neq 0$, and the motion is off the high-symmetry direction, this is no longer true, and the two exciton bands will interact and mix strongly giving rise to the nonparabolicity and the mass reversal predicted by Kane.[1,2]

We have determined the eigenvalues of Eq. (3) at various values of the translational momentum $\vec{k}$, thus obtaining explicitly the dispersion curves. These calculations are considerably more complicated than those for the $k=0$ case, and, to keep their size within reasonable limits, we did not include $L=4$ terms in the eigenfunction expansion. The effect of g-like-function admixture, however, can be estimated in the following way. A phenomenological analytical expression for the exciton dispersion was proposed in Ref. (1):

$$E_\pm(\vec{k}) = E_s + \frac{\hbar^2}{2m_0}(r_{ls}k_l^2 + r_{ts}k_t^2) \pm \left[A^2 + \left(\frac{\hbar^2}{2m_0}\right)^2 (r_{tc}^2 k_t^4 + r_{mc}^2 k_t^2 k_l^2)\right]^{1/2}, \tag{4}$$

where

$$A = E_d + (\hbar^2/2m_0)(r_{ld}k_l^2 + r_{td}k_t^2). \tag{5}$$

This dispersion relation corresponds to two exciton bands with parabolic dispersion interacting via off-diagonal terms $r_{tc}k_t^2$ and $r_{mc}k_lk_t$, and provides a satisfactory interpolation of our numerical results, with the parameters listed in Table II. We then obtain the E_s and E_d values from our $\vec{k}=0$ calculation, which includes g-like terms, and assume that the translational masses are not very sensitive to this small correction in the binding energies at $\vec{k}=0$.

The dispersion curves, in the region of the k space corresponding to an exciton kinetic energy of ≲ 1–2 meV are not very sensitive to the value of the parameter r_{mc}, so that we cannot determine it with the same accuracy of the other parameters, but can only establish that it is small; the value appearing in Table II is to be understood as an upper limit.

The theoretical dispersion curves are shown in Fig. 1 for the transverse direction. The interaction and subsequent repulsion of the two branches

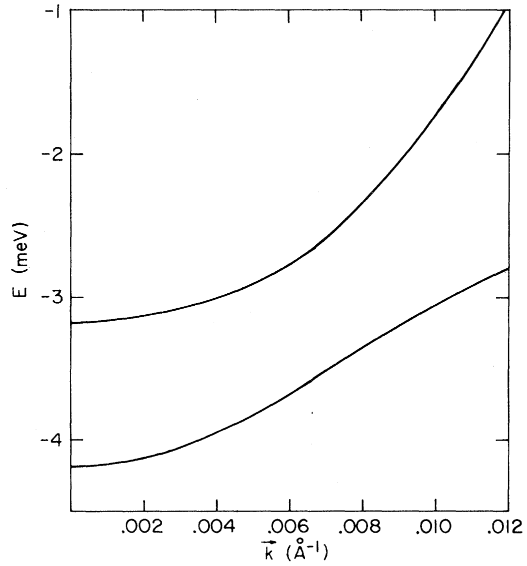

FIG. 1. Energy-momentum dispersion of the two 1s excitons in Ge in the transverse direction, i.e., for $\vec{k} \perp \langle 111 \rangle$.

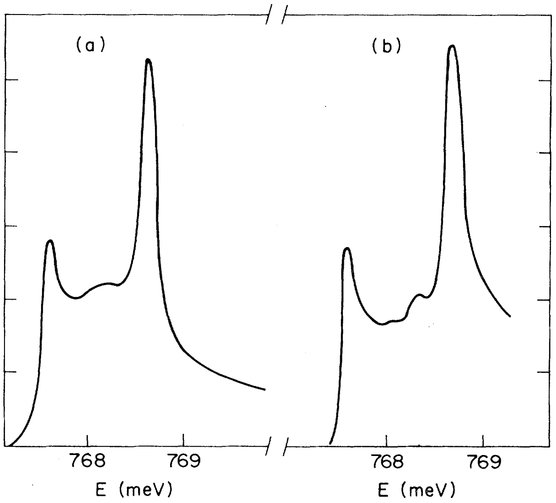

FIG. 2. Curve *a*, experimental wavelength-modulated optical absorption in Ge in the LA-assisted transition region, from Ref. (1) (arbitrary units). Curve *b*, derivative of the density of states, computed from the theoretical dispersion curves (arbitrary units).

is self-evident. We mention that a small, but appreciable, nonparabolicity is also displayed by the numerical results for the longitudinal direction.[7]

We now address ourselves to the problem of the optical line shape resulting from the energy-momentum dispersion. In Fig. 2, we show the derivative of the density of states corresponding to the theoretical dispersion curves (Gaussian broadened to match experimental resolution), and, for comparison, the modulated absorption coefficient due to LA-phonon-assisted transitions to indirect excitons, measured by Frova *et al.*[1] The agreement between the two curves is very good, especially when one considers that the theoretical curve contains no adjustable parameters, and that matrix-element effects were not considered. Notice that the theoretical curve shows a double structure between the two main peaks, rather than the single broad hump appearing on the experimental curve. The existence of a weak double structure, however, cannot be completely ruled out[8] by the experiment described in Ref. 1.

In conclusion, we wish to summarize the main results reported in this Letter. It was shown that an effective-mass calculation accurately reproduces the experimental values for the binding energies of indirect excitons in Ge, and can be extended to the calculation of energy-momentum dispersion relations which allow a quantitative understanding of the optical line shape.

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