band gap of 1.0 Ry is obtained for an exchange parameter of 0.95 while an exchange parameter of 1.06 gives the experimental gap for NaF.

The bands in Fig. 2 were obtained using an 89point equal-volume-weight grid¹ in $\frac{1}{48}$ of the Brillouin zone to compute new charge densities for successive iterations. Self-consistent energy bands were also calculated using 20-, 6-, 5- and 4point equal-volume-weight grids and 6- and 4point nearest-volume-weight grids.^{4,5} The 5-point equal-volume-weight grid is the one used by Chaney et al.³ and the 6- and 4-point nearestvolume-weight grids are the ones used by Stukel et al. The points and weights reported by Stukel and Euwema for the 6-point nearest-volumeweight grid are the same as those used in the 6point equal-volume-weight grid, while the 4-point equal- and nearest-volume-weight grids have the same points but different weights. Table I shows the results obtained using the different types of grids. The band gaps or energy differences do not change by more than a few hundredths of a rydberg in going from 4, 5, or 6 points to 89 points, but

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PHYSICAL REVIEW B

the actual position of the bands relative to vacuum changes by as much as several tenths of a rydberg. Similar results were found for NaF. Thus it appears that 4-, 5-, or 6-point grids give reasonably accurate energy differences, but the actual position of the bands may differ by as much as 3 or 4 eV from results obtained using a larger Brillouinzone sampling.

Figure 3 shows the change in the electronic charge density from the first to the final (selfconsistent iteration). Self-consistency causes negative charge to be removed from the interstitial regions and placed in the region around the F ion (also a very small amount is placed near the Li ion). An approximate value for the amount of charge moved to the F site can be obtained by assuming that the change in the charge density is spherically symmetric near the ions and then doing a spherical-volume integral from the F ion out to the point where the change in the charge density goes through zero. The result is that approximately 0.46 electron is moved to the F site.

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Electron-Hole Drops in Pure Ge

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The binding energy of electron-hole drops in pure Ge is obtained from their luminescence spectrum, and some information on the exciton-drop phase diagram is given. We show, in addition, that experimental data indicate that electron-hole correlations are probably important in this condensed phase. Finally, a new method is used to get the critical density in these drops.

I. INTRODUCTION

In a previous paper, ¹ we studied the condensation of free excitons (FE) into electron-hole drops (EHD) in pure Ge. We report here additional data concerning the EHD binding energy and the FE-EHD phase diagram in this material. Moreover, we discuss experimental results suggesting that electron-hole correlations are probably important in EHD. Finally, we describe a new method allowing us to determine experimentally the EHD critical density in pure Ge.

II. DETERMINATION OF EHD BINDING ENERGY

Our previous experimental determination¹ of the EHD binding energy $\langle E_n \rangle_m - E_g$ is not correct, and we wish to describe a better method to get this energy at low temperature. First, let us consider the system represented in Fig. 1. It is constituted by N electron-hole pairs in a volume



FIG. 1. System constituted by N/V electrons in the conduction band and N/V holes in the valence band.

 V_{2} , and its total energy E can be written E = Nf(N/V), so that the corresponding chemical potential W is

$$W = \frac{dE}{dN} = f\left(\frac{N}{V}\right) + \left|N\frac{df(N/V)}{dN}\right|.$$
 (1)

In an EHD, the mean energy per pair is minimum, so that df(N/V)dN = 0 and, in this case, $W = f(N/V) = \langle E_n \rangle_m$.

Moreover, the shape $I_{LA}(h\nu)$ of the LA-phononassisted emission line of EHD in Ge can be calculated easily at T = 0. This line shape is given by Eq. (10) of Ref. 1 and the results of this calculation, which are represented in Fig. 2 for $n_c = 2.6 \times 10^{17}$ cm⁻³, are in good agreement with the experimental data. It must be pointed out that this method has been used by Pokrovsky *et al.*² to obtain the first experimental value of n_c . Moreover, it is also possible to determine theoretically $I_{LA}(h\nu)$ at a finite temperature. In this case, if E_e and E_h are the energies of electrons and holes in the conduction and valence bands, $I_{LA}(h\nu)$ can be written

$$I_{\text{LA}}(h\nu) = \alpha \int_0^\infty \int_0^\infty n(E_e) n(E_h) f(E_e) f(E_h)$$
$$\times \delta(h\nu - E_g - E_e - E_h + \hbar\omega) dE_e dE_h , \qquad (2)$$

where α is a constant and $n(E_e)$, $n(E_h)$, $f(E_e)$, and $f(E_h)$ are, respectively, the state densities in the conduction and valence bands and the Fermi distribution functions of electrons and holes in the same bands.

Figure 2 gives the theoretical line shape $I_{LA}(h\nu)$ at 2 °K in Ge, and it can be seen that experiment and theory are also in good agreement for $n_c = 2.6 \times 10^{17}$ cm⁻³. In fact, this is not surprising because, for a given value of the density, the corresponding electron and hole Fermi levels E_F^e and E_F^h do not vary appreciably in the temperature range studied here. Since the energy $E_A + E_{LA}$ (see Fig. 2), where E_{LA} is the energy of the LA phonon, is obviously equal to W at T = 0, we can conclude that $E_A + E_{LA}$ is also equal to W, and therefore to $\langle E_n \rangle_m$, at 2 °K, so that it is possible to get $\langle E_n \rangle_m$ from the experimental luminescence spectrum of EHD. Indeed, as shown in Fig. 2, E_A can be easily obtained by extending the linear part of the highenergy side of the experimental EHD LA-phononassisted line (hereafter called *B*) down to its intersection with the energy axis.³

Now, if $E_{\text{FE}} - E_{\text{LA}}$ is the energy of the LA-phonon-assisted emission line of FE, we get experimentally $\phi = E_{FE} - \langle E_n \rangle_m \sim 2.4 \text{ meV}$ and $\langle E_n \rangle_m - E_g$ $= -\phi - R^{*} \sim -6$ meV, since $E_{FE} - E_{LA} \sim 713.6$ meV, $E_{A} \sim 711.2$ meV, and $R^{*} = 3.6$ meV.⁴ Let us note that Brinkman et al.⁵ and Combescot and Nozières⁶ find, respectively, -5.3 and -6.1 meV for $\langle E_n \rangle_m - E_g$. It is also noteworthy that Pokrovskii and Svistunova⁷ have determined ϕ with another method which yields $\phi \sim 2.7$ meV, but this value must be slightly corrected. Indeed, to obtain ϕ from their data, they have plotted g/T^2 as a function of 1/T, but it is in fact more correct to plot $g/T^{3/2}$ vs 1/T because v, which is the FE thermal velocity, is proportional to $T^{1/2}$. If we take this remark into account, we find $\phi \sim 2.8$ meV from the results described in Ref. 7. Now, if we use our experimental value of $\langle E_n \rangle_m - E_g$ and the data given in Table I of Ref. 1, we can determine easily the mean correlation energy $\langle E_{cor} \rangle$. This quantity is found to be equal to -4.55 meV in Ge instead of -6.75 meV as stated in our previous paper.¹

If we use the same method in Si, we obtain from





the experimental results of Haynes⁸ $\phi \sim 7$ meV, so that $\langle E_n \rangle_m - E_g \sim -21.7$ meV since $R^* = 14.7$ meV.⁹ It can be noticed that the theoretical values of $\langle E_n \rangle_m - E_g$ which are now available in Si are -21^6 and -21.5 meV.¹⁰ We thus get $\langle E_{cor} \rangle \sim -16.3$ meV instead of -24.3 meV¹ if we use again the data reported in Table I of Ref. 1.

III. PHASE DIAGRAM

We now wish to give some information, in the case of pure Ge, on the FE-EHD phase diagram which is sketched in Fig. 2 of Ref. 1. At first we observed that the half-width of the *B* line does not depend on *T* for temperatures between 1.7 and 4.2 °K, so that the critical density n_c in EHD is approximately constant in this temperature range. In fact, it is likely that n_c is modified only when *T* is near the critical temperature T_c .

Moreover, if we assume that FE behave like a perfect gas, it is possible to calculate the density n_s of the FE gas at saturation which corresponds to the lower branch of Fig. 2 in Ref. 1. Indeed, if W and W' are, respectively, the chemical potentials of EHD and FE, the following relation can be written¹¹:

$$W = W' = E_{\rm FE} + kT \ln\left[\frac{n_s}{32} \left(\frac{2\pi\hbar^2}{mKT}\right)^{3/2}\right],$$
 (3)

where $E_{\rm FE}$ is the FE energy and

$$2m = [(m_{hh} + m_{e1})^2 (m_{e11} + m_{hh})]^{1/3} + [(m_{h1} + m_{e1})^2 (m_{e11} + m_{h1})]^{1/3} .$$

Here¹² m_{hh} and m_{hl} are the effective masses of heavy and light holes, while m_{ell} and m_{el} are the longitudinal and transverse effective masses of electrons. Let us add that we have taken into account the FE degeneracy in Eq. (3). Since $W - E_{\rm FE}$ = $-\phi = -2.4$ meV, relation (3) yields $n_s \sim 1.5 \times 10^{11}$ cm⁻³ at 2 °K and $n_s \sim 5 \times 10^{14}$ cm⁻³ at 4.2 °K.

It is noteworthy that it is also possible to determine the concentrations n of free-electronhole pairs and $n_{\rm EM}$ of excitonic molecules (EM) coexisting with the gaseous phase of FE whose density is n_s . Indeed, if N_c , N_v , $N_{\rm FE}$, and $N_{\rm EM}$ are, respectively, the effective state densities for electrons, holes, FE, and EM, the law of mass action gives

$$n^{2} = (N_{c}N_{v}/N_{FE})n_{s} e^{-R^{\mp}/KT}$$
(4)

and

$$n_{\rm EM} = (N_{\rm EM} n_s^2 / N_{\rm FE}^2) e^{B^* / KT}$$
, (5)

where B^* is the binding energy of EM.

At 4.2 and 2 °K, we thus find, respectively, $n \sim 5.4 \times 10^{12}$ and 2.8×10⁸ cm⁻³. For the same temperatures, we obtain $n_{\rm EM} \sim 1.2 \times 10^{13}$ and 4×10⁶ cm⁻³ if we give to B* the value calculated recently by Akimoto and Hanamura, 13 i.e., 0.075 meV. These results show, therefore, that it is reasonable to neglect free-electron-hole pairs and EM in the study of the condensation of FE into EHD.

IV. EHD RADIATIVE LIFETIME AND ELECTRON-HOLE CORRELATIONS

We must begin by pointing out that one of our previous determinations¹ of the critical density n_c in EHD is not valid. ¹⁴ Indeed, we have deduced n_c from the ratio of the FE and EHD radiative lifetimes $\tau_R^{\text{FE}}/\tau_R^{\text{EHD}}$, which is proportional to $|\phi_{\text{FE}}(0)|^{-2}$, but we have taken $|\phi_{\text{FE}}(0)|^2 = 1/64 \pi a_0^3$ instead of $1/\pi a_0^3$. For this reason the value of n_c given by this method is in fact too large, but these results seem to indicate that electron-hole correlations may be important in EHD.

In this case, by analogy with positron annihilation in metals, ¹⁵ we think that the EHD radiative recombination probability $|\gamma|^2$, which is given by Eq. (12) of Ref. 1, must be multiplied by an enhancement factor ρ , so that $|\gamma|^2$ can be written¹⁶

$$|\gamma|^{2} = \left(\left| D \right|^{2} / \left| \Delta E \right|^{2} \right) \left| H \right|^{2} \rho n_{c} .$$

$$\tag{6}$$

We assume here that ρ is k independent, so that it does not affect the EHD emission line shapes. For the same reason, this enhancement factor does not modify the ratio $I_{\rm TA}/I_{\rm LA}$ of the intensities of the A and B lines, where A corresponds to the TAphonon-assisted emission line of EHD.

Moreover, from $|\gamma|^2$ and from Eq. (14) of Ref. 1, it is possible to get $\tau_R^{\text{FE}}/\tau_R^{\text{EHD}}$, which can be written

$$\tau_{R}^{FE} / \tau_{R}^{EHD} = \rho n_{c} / \left| \phi_{FE}(0) \right|^{2} , \qquad (7)$$

where $|\phi_{\rm FE}(0)|^2 = 1/\pi a_0^3 \sim 1.5 \times 10^{17} {\rm cm}^{-3}$ in Ge, since $a_0 = e^2/2\epsilon R^* \sim 130$ Å if we take $R^* = 3.6$ meV.⁴ In pure Ge, $n_c \sim 2 \times 10^{17} \text{ cm}^{-3}$, ¹ and we have found experimentally $\tau_R^{\text{FE}}/\tau_R^{\text{EHD}} \sim 16$, so that ρ is of the order of 12. If we use the theoretical data of McLean and Loudon, ¹⁷ i.e., $a_0 = 120$ Å and $|\phi_{\rm FE}(0)|^2 = |\beta|^2 / \pi a_0^3$, where $|\beta|^2 = 0.85$, ¹⁸ we also find $\rho \sim 12$. However, it must be pointed out that our result is not very accurate, for several reasons. First, the FE Bohr radius is not well known in Ge and, in addition, our experimental value of $\tau_R^{\rm FE}/\tau_R^{\rm EHD}$ may be too large by a factor of 2, essentially because it is difficult to measure precisely the FE total lifetime whose knowledge is necessary to get $\tau_R^{\rm FE}/\tau_R^{\rm EHD}$ from our experimental results.¹ Indeed, in the case of FE, the radiative efficiency is rather low and the signal-to-noise ratio is not very good. Besides, our determination of ρ neglects¹⁹ completely the thermal dissociation of FE at 20 $^{\circ}$ K. If this effect could be taken into account, $\tau_{R}^{\rm FE}/\tau_{R}^{\rm EHD}$ would certainly be decreased, so that ρ would be smaller. Unfortunately, it seems difficult to determine unam-



FIG. 3. Experimental and theoretical line shapes of the TA-phonon-assisted emission line of EHD in pure Ge.

biguously the influence of the thermal dissociation of FE on our data.

Finally, it is noteworthy that calculations due to Brinkman and Rice²⁰ show that ρ is of the order of 3, so that there is at the present time a discrepancy between experiment and theory. We think that it is very important to improve the accuracy of our measurement method of the enhancement factor because the comparison of the experimental and theoretical values of ρ provides a very good test of the validity of the calculations which have been done on EHD.^{5,6,10} For this reason, we intend to study τ_{R}^{FE} near the critical temperature; we believe that this will allow us to obtain a better result for ρ . Indeed, as can be deduced from the data given in Sec. III, the density of free-electronhole pairs is in this case smaller than n_s , so that the thermal dissociation of FE can be neglected.

V. CRITICAL DENSITY IN EHD

To determine the critical density n_c in pure Ge, we use here a method based on the shape of the

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EHD TA-phonon-assisted emission line. As shown in Fig. 4 of Ref. 1, this line and the B line have different shapes because, contrarily to the B line, the A line corresponds to a recombination process which is forbidden for an electron-hole pair at the band extrema.²¹ If we make the same assumptions as in Ref. 1, the shape $I_{TA}(h\nu)$ of the A line can be written at T = 0

$$I_{\mathrm{TA}}(\hbar\nu) = \frac{|D|^2}{|\Delta E|^2} M_{ee}^2 \int_{\nu_h} \int_{\nu_e} k_{ee}^2 \times \delta(\hbar\nu - E_g - E_{\mathrm{kin}}^e - E_{\mathrm{kin}}^h + \hbar\omega) d\vec{\mathbf{k}}_e d\vec{\mathbf{k}}_h .$$
(8)

We have used this expression to calculate the shape of the A line, and we have found a good fit between experiment and theory for $n_c \sim 1.8 \times 10^{17}$ cm⁻³ as shown in Fig. 3. Let us only note that this value is in good agreement with the other determinations of n_c which are reported in Ref. 1.

VI. CONCLUSION

Finally, we just want to emphasize that the experimental and theoretical results obtained for the binding energy of EHD are in good agreement and also that electron-hole correlations are certainly important in EHD. However, there is at the present time a discrepancy between experiment and theory on the value of the enhancement factor corresponding to these electron-hole correlations, and it is thought that it would be interesting to improve the accuracy of the experimental determination of this factor.

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Rept. Progr. Phys. 31, 533 (1968), and references therein.

¹⁶It is obvious that Fig. 5 of Ref. 1 gives now the variation of ρn_c with the applied uniaxial pressure P. However, the introduction of this enhancement factor does not modify the interpretation of our stress experiments. In particular, we can certainly neglect the

PHYSICAL REVIEW B

variation of ρ with P as long as n_c is not very much decreased.

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Equivalence of Two Approaches to the Random Chain of Oscillators^{*}

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The spectrum and localization length of certain one-dimensional disordered systems can be found either by a node-counting technique, or by a recently proposed Green's-function method. We prove here the mathematical equivalence of the two approaches.

I. INTRODUCTION

Several one-dimensional problems in the theory of disordered materials can be reduced to the diagonalization of a tridiagonal matrix. Examples are the chain of oscillators with random masses or spring constants, ^{1,2} an electron in a set of nonoverlapping potential wells^{3,4} located at random, and the tight-binding nearest-neighbor hopping model for an alloy.^{5,6} An exact expression for the integrated density of states N(E) for this problem has first been given by Dyson, and reformulated by Schmidt.² The underlying idea is that the nth eigenfunction of a one-dimensional Schrödinger equation has (n-1) zeros in the interior of the region of interest; thus, finding N(E) is reduced to a problem of node counting. By differentiation it is then possible to find the density of states $\rho(E)$ = dN/dE, which is usually the quantity of interest. There appears however a practical difficulty when these calculations are carried out: The nodecounting problem involves the numerical solution of an integral equation, which is usually done by iteration on a computer. This means that N(E) is known with a small error which varies in an uncontrolled way from one energy to the next, and which makes it difficult to get reliable values for $\rho(E)$.

Recently Economou and Cohen,⁵ and Economou and Papatriantafillou⁶ have come up with an approach based on a Green's-function technique, and which is free of the above difficulty. They obtained an equation which gives $\rho(E)$ directly, an obvious

advantage for numerical work. In addition, the Green's-function treatment can easily be generalized to include, for example, second-nearestneighbor hopping, while there is no natural way of carrying out such a generalization from the nodecounting point of view.

The object of this work is to prove the equivalence of the two approaches for those problems to which both apply. This may seem logically unnecessary, since both provide exact solutions to the same problem; but the fact that their derivations are based on certain assumptions (e.g., ergodicity) which have not been rigorously proved, makes it desirable to have a direct check of the results arrived at by both methods.

To avoid unessential complications, we consider one particular problem: the tight-binding nearestneighbor-hopping-only alloy with randomness restricted to the diagonal elements. With slight changes in notation, the proof applies to all other situations.

We start by stating the problem, then by giving the set of equations describing it in the node-counting approach, by giving the set of equations describing it in the Green's-function approach, and finally by showing that the results are equivalent.

II. FORMULATION OF PROBLEM

Consider a set of orbitals $\{|n\rangle\}$ located along a line. Let the Hamiltonian be

1

$$H = \sum_{n} |n\rangle \epsilon_{n} \langle n| - V \sum_{n,m}' |n\rangle \langle m| , \qquad (1)$$