Dielectric-constant enhancement as the insulator-metal transition is approached from the insulating side

T. G. Castner
University of Rochester, Rochester, New York 14627
(Received 24 October 1978)

A comparison of the dielectric-constant-enhancement theory of Leroux Hugon and Ghazali with previous experimental data shows their calculated N_c nearly a factor of 3 too small, thus giving less than satisfactory agreement with experiment. Questions about the adequacy of their theoretical approach are also discussed.

Recently Leroux Hugon and Ghazali[1,2] have given a theory of the dielectric constant enhancement as $N \to N_c$ (N_c is the critical concentration for the onset of metallic behavior) in an attempt to explain our earlier experimental data.[3] Leroux Hugon and Ghazali employ a variational approach and a Hartree-like approximation to calculate the multiplicative dielectric constant enhancement, $\epsilon(n)$ [the actual dielectric constant is $\epsilon(n)\kappa$, where κ is the host dielectric constant] and claim to obtain good agreement with the data.[3] This Comment shows that their results are not in good agreement with the data, and, in addition, raises questions about the adequacy of their theoretical model.

Leroux Hugon and Ghazali show in their Fig. 1 $\epsilon(n)$ vs n [$n = N/N_0$, where $N_0 = \pi/3(4a_0^*)^3$ and $a_0^* = \kappa\hbar^2/m^*e^2$] and obtain $n_c = 0.61$. Using the best values[4] of $\kappa = 11.4$, $m^*/m = 0.299$, and therefore $a_0^* = 20.18$ Å, one thereby obtains $N_c = 0.61\ N_0 = 1.2 \times 10^{18}/\text{cm}^3$. This is nearly a factor of 3 smaller than the experimental values[3] for Sb- and P-doped Si, which are $(3.0 \pm 0.2) \times 10^{18}/\text{cm}^3$ and $(3.5 \pm 0.4) \times 10^{18}/\text{cm}^3$, respectively (as is even larger).

In Fig. 1 the Leroux Hugon and Ghazali $\epsilon(n)$ curve is shown versus the actual concentration and compared with the experimental data. By using a much smaller isotropic Bohr radius ($a_0^* = 14.66$ Å) the Leroux Hugon and Ghazali value of N_c could be increased by a factor of 2.6, thereby bringing their enhancement curve up to the values of the P and Sb data. However, there is no justification for such a small Bohr radius, especially since Leroux Hugon and Ghazali neglect central-cell corrections and their Bohr radius is an isotropic effective-mass-approximation (EMA) value. Leroux Hugon and Ghazali do not give numbers for the important parameters in their paper.

Rather poor agreement would also be obtained by using the Clausius-Mossotti or Herzfeld criterion $N_c = 3\kappa/4\pi\alpha_D$ and the measured donor polarizibilities.[4] In this case the donor-dependent values of N_c are more than a factor of 3 larger than the accepted values of N_c. The data,[3] however, showed substantial upward deviations from Claudsius-Mossotti behavior as $N \to N_c$. We suggested[3] that one possible explanation for this was an increase in $\alpha_D(N)$ as $N \to N_c$. The Leroux Hugon and Ghazali calculation implicitly contains this polarizability enhancement but it is not explicitly shown in Ref. 1. Using $\epsilon(N) = 1 + 4\pi N\alpha/(1 - 4\pi N\alpha/3)$ and the zero-wave-number polarizability $\alpha(q = 0, N = 0) = \frac{9}{2}a_0^{*3}$ (κ deleted from α) one obtains $\epsilon(n) = 1.547$ at $n = 0.5$ and $\epsilon(n) = 1.695$ at $n_c = 0.61$. From the Leroux Hugon and Ghazali values in Fig. 1 of $\epsilon(n) \sim 1.62$ at $n = 0.5$ and $\epsilon(n) = 2.7$ at $n_c = 0.61$ one can infer that Leroux Hugon and Ghazali obtain polarizability enhancements $\alpha(n)/\alpha(0)$ of 1.11 and 1.92 at $n = 0.5$ ($0.82\,N_c$) and $n_c = 0.61$, respectively. The experimental enhancement values for Si:As

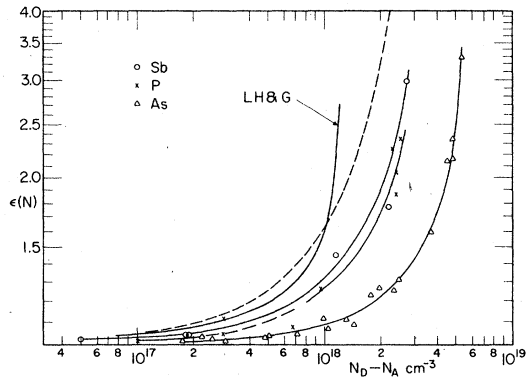

FIG. 1. Comparison of the multiplicative dielectric enhancement calculated by Leroux Hugon and Ghazali and the experimental data for As, P, and Sb donors in silicon. Note that the experimental dielectric constants are normalized to $\kappa = 11.4$. The dashed curve is the result from a new theory (Ref. 10) for $\epsilon(N)$ for the special case when central-cell and many-valley corrections are neglected.

are close to 2 at $0.82N_c$ and would have to be nearly 4 to explain the value of N_c for Si:As.

The important reasons for the differences between the experimental results and the calculated results of Leroux Hugon and Ghazali are: (i) their neglect of the central cell $V(r)$ which substantially reduces the $\alpha_D(0)$ values below the isotropic effective-mass value $\alpha_{\rm EMA} = \frac{9}{2}\kappa a_0^{*3}$ and (ii) their use of a perturbation theory expression for $\alpha(q, N)$ and the inclusion of only the $n=2$ excited states. The experimental values[5] of $\alpha_D(0)$ for Sb, P, and As donors in Si are, respectively, 0.72, 0.55, and 0.23 of the $\alpha_{\rm EMA}$ value 4.32×10^{-19} cm^3 calculated by Dexter.[6] Dexter's calculation takes into account the mass anisotropy [$\alpha_{\rm EMA} = \frac{1}{3}(\alpha_l + 2\alpha_t)$]. The greater the reduction of $\alpha_D(0)$ below $\alpha_{\rm EMA}$ the greater the increase in N_c. The employment of only the $n=2$ excited states in the perturbation expression for $\alpha(q, N)$ can hardly be expected to give reliable values of $\alpha(0, N)$ and the polarizability enhancement. It is well known for an isolated hydrogenic atom that the $1s \rightarrow 2p$ transition accounts for 41.6% of the total oscillator strength while the continuum accounts for 43.5%. It is not known how these percentages would change as $n \rightarrow n_c$ when donor-donor interactions become of paramount importance. However, it would not be surprising if the perturbation expression with only $n=2$ excited states substantially underestimated the polarizability enhancement. A variational approach expression for $\alpha(N)/\alpha(0)$ might be expected to be more reliable.

In Ref. 2 Leroux Hugon and Ghazali give an expression [their Eq. (6)] for the Clausius-Mossotti factor $[\epsilon(0)-1]/[\epsilon(0)+2] = C$ of the form $C \propto x_m^2 n/(\epsilon_{2p} - \epsilon_{1s})$ based on their expression for $\alpha(0, n)$. They assert that $x_m = a^*(n)/a^*(0)$ makes only a minor contribution to the polarizability enhancement and that most of the enhancement comes in the reduction in the energy denominator $\epsilon_{2p} - \epsilon_{1s}$ as n increases toward n_c. Their Fig. 2 shows ϵ_{1s} decreasing to $\frac{1}{2}$ its $n=0$ value while the ϵ_{2p} value appears to be virtually independent of n up to n_c. This results in a threefold reduction in $\epsilon_{2p} - \epsilon_{1s}$ and at least a threefold enhancement in α as $n \rightarrow n_c$, although this appears to be larger than the enhancement inferred from Fig. 1 in Refs. 1 and 2. The lack of any significant change of ϵ_{2p} with n is rather surprising since the donor-donor interactions might be expected to weaken the binding of the more extended $n=2$ excited states before affecting the $1s$ state. There is no experimental evidence that the $1s$-$2p$ transition energy of shallow donors in Si is reduced by a factor of 3 as $n \rightarrow n_c$. A recent infrared absorption study by Townsend[7] on Si:P samples as $n \rightarrow n_c$ shows no lowering of the $1s$-$2p_0$ transition energy with increasing doping comparable to the Leroux Hugon and Ghazali result. The screening of the Wannier exciton state transitions as the metallic transition is approached in Hg-Xe mixtures as observed by Raz *et al.*[8] also shows very little shift of the $n=1$ exciton peak with concentration as $n \rightarrow n_c$. For these reasons we suggest that Leroux Hugon and Ghazali have substantially overestimated the reduction in $\epsilon_{2p} - \epsilon_{1s}$ and thereby overestimated the polarizability enhancement resulting from the $2p$ contribution.

In their reply (following paper) to this Comment Ghazali and Leroux Hugon suggest that the central-cell correction (CCC) proposed here will not give an adequate correction to their theory. In support of this view they argue that the results of Lipari and Dexter[9] for $\alpha_D(0)$ in their calculation of $\alpha_D(H)$ are in rather poor agreement with experiment. Lipari and Dexter find an average comparison $\langle\alpha_D(0)\rangle = 0.58\langle\alpha_{D\,\rm expt}\rangle$ for the three donors Sb, P, and As in Si; however, these authors caution against a close comparison with experiment because of the crude form of the CCC employed in their calculation. It is worth noting that another theory[10] has been developed of $\alpha_D(N)$ which includes a somewhat better CCC and also includes the many-valley contribution. This new theory employs an expression for $\alpha_D(0)$ which would be exact for a spherical hydrogenic wave function. The single valley energy correction[11] to EMA theory is employed to determine a single screening parameter in the central-cell potential and the many-valley correction is added in a phenomenological way. My theory yields $\alpha_D(0)$ values of $0.52\alpha_{\rm EMA}$, $0.41\alpha_{\rm EMA}$, and $0.32\alpha_{\rm EMA}$ ($\alpha_{\rm EMA}$ is Dexter's value from Ref. 6) for Sb, P, and As, respectively, which gives $\langle\alpha_D(0)\rangle = 0.94\langle\alpha_{D\,\rm expt}\rangle$ for these three donors. This is an improvement on the results of Lipari and Dexter, but one should note that the calculated values of $\alpha_D(0)$ for Sb and P are somewhat too small and that for As is slightly large when compared with experiment. Finally, it should be mentioned that the experimental error bars for $\alpha_D(0)$ are still fairly large and could be as large as 20% for individual cases. At the present time no theory of $\alpha_D(0)$ has been given which takes account of the full complexity of the central-cell potential. Nevertheless, we still maintain the central-cell correction is the most important single correction that would bring the dielectric enhancement theory of Leroux Hugon and Ghazali into better agreement with the experimental values of N_c.

In order to facilitate a comparison between the results of Leroux Hugon and Ghazali and my theory for the case without any CCC and any many-valley contribution Fig. 1 shows $\epsilon(N)$ (dashed curve) calculated with an accurate expression for

$\alpha(N)$ employing a somewhat different donor-donor interaction potential than Leroux Hugon and Ghazali. One observes that the two theoretical curves cross. At low concentrations the Leroux and Ghazali result lies below the dashed curve, while at larger N the Leroux Hugon and Ghazali $\epsilon(N)$ rises more rapidly than the dashed curve. Two comments are in order. The shape of the dashed curve seems to fit more closely to the experimental curves than the Leroux Hugon and Ghazali curve, which seems to rise too steeply as $N \to N_c$. Their curve rises too rapidly because their $\epsilon_{2p} - \epsilon_{1s}$ energy drops too rapidly with N as already mentioned. The second and important point of difference concerns the nature of the phase transition. Leroux Hugon and Ghazali view the transition as first order and $\epsilon(N)$ remains finite as $N \to N_c$ $[\epsilon(N_c) = 2.7]$ while we view the transition as second order and obtain N_c from the polarization catastrophe criterion $\epsilon(N) \to \infty$ $[4\pi N_c \alpha(N_c)/3\epsilon_0 = 1]$ from the Clausius-Mossotti expression (this yields $N_c = 3.3 \times 10^{18}/\mathrm{cm}^3$). As the central-cell potential is added to the theory it reduces $\alpha_D(0)$ substantially below α_{EMA} and shifts the $\epsilon(N)$ curve to larger N, but without appreciably altering the shape of the curve. The divergence of the dielectric enhancement $\epsilon(N)$ as $N \to N_c$ corresponds to the vanishing of the Hubbard gap and the conductivity activation energy ϵ_2. At present the maximum observed values of $\epsilon(N)$ are only slightly larger than $\epsilon(N_c) \sim 2.7$ obtained by Leroux Hugon and Ghazali. With very high quality, macroscopically homogeneous samples with negligible compensation experiments in the mK range may be able to establish whether $\epsilon(N)$ continues to rise, or whether it reaches a maximum for $N \lesssim N_c$.

Very recently Ghazali and Leroux Hugon[12] have applied a density functional approach to the metal-insulator transition in doped semiconductors. Whatever the merits of this new approach it is important to compare its result with experiment. Ghazali and Leroux Hugon find $N_c = 0.28N_0 = 5.57 \times 10^{17}/\mathrm{cm}^3$ for the isotropic EMA value of $a_0^* = 20.18$ Å. This new result is nearly a factor of 6 below the experimental values and more than a factor of 2 below the earlier result $N_c = 0.61N_0$ obtained by these authors. On the other hand, my theory[10] yields results for N_c which average 47% larger than the experimental N_c values for Sb, P, and As in Si. This theory gives a good account of the donor dependence of N_c and supports the idea of a smooth second-order transition at 0 K.

In summary it is argued that the Leroux Hugon and Ghazali calculations are not in very good agreement with the data and that a theory taking account of central-cell corrections and employing a reliable expression for $\alpha_D(N)$ is required.

ACKNOWLEDGMENT

This work has been supported in part by NSF Grant DMR77-20450.

[1] P. Leroux Hugon and A. Ghazali, Phys. Rev. B 14, 602 (1976).
[2] P. Leroux Hugon and A. Ghazali, J. Phys. (Paris) Colloq. Suppl. 4, 323 (1976).
[3] T. G. Castner, N. K. Lee, G. S. Cieloszyk, and G. L. Salinger, Phys. Rev. Lett. 34, 1627 (1975).
[4] R. A. Faulkner, Phys. Rev. 184, 713 (1969). The $E_{1s\text{-}\mathrm{EMA}} = 31.27$ meV value yields an isotropic $m^*/m = 0.299$.
[5] J. Bethin, T. G. Castner, and N. K. Lee, Solid State Commun. 14, 1321 (1974).
[6] D. L. Dexter, *Proceedings of the Thirteenth International Conference on the Physics of Semiconductors, Rome, 1976* (North-Holland, Amsterdam, 1976), p. 1137.
[7] P. Townsend, J. Phys. C 11, 1481 (1978).
[8] B. Raz, A. Gedanken, U. Even, and J. Jortner, Phys. Rev. Lett. 28, 1643 (1972).
[9] N. O. Lipari and D. L. Dexter, Phys. Rev. B 18, 1346 (1978).
[10] T. G. Castner, Solid State Commun. (to be published).
[11] For a review and discussion of these quantities see E. B. Hale, J. Phys. Chem. Solids 34, 621 (1973).
[12] A. Ghazali and P. Leroux Hugon, Phys. Rev. Lett. 41, 1569 (1978).