Direct Observation of the Hubbard Gap in a Semiconductor

O. D. Dubon,[1,2] W. Walukiewicz,[2] J. W. Beeman,[2] and E. E. Haller[1,2]

[1]*University of California, Berkeley, California 94720*
[2]*Lawrence Berkeley National Laboratory, Berkeley, California 94720*

The transformation of the ground state of Cu acceptors in uniaxially stressed Ge from the $(1s)^3$ to the $(1s)^2(2s)^1$ configuration results in a unique system in which a highly delocalized hole wave function corresponds to a relatively deep electronic state. This leads to electronic conduction via an isolated impurity band within the Ge band gap. By changing the Cu concentration we observe an evolution of the Hubbard gap for the $2s$ state from the full gap of 3.7 meV at 3×10^{14} cm^{-3} to zero gap at 1.6×10^{16} cm^{-3}, in good agreement with our calculations. [S0031-9007(97)03085-8]

Understanding the phenomena associated with a transition from localized atomlike to extended metal-like electronic states in solid-state systems has been one of the most difficult and extensively studied problems in condensed matter physics [1,2]. With an unmatched control of the concentration of electrically active impurities, intentionally doped semiconductors are excellent model systems that have been the focus of numerous studies concerned with fundamental electronic transport processes including hopping conduction [3] and the metal-insulator transition (MIT) [4–6]. Thus far most of these studies have been limited to shallow hydrogenic dopants with relatively large ground-state Bohr radii. Attempts to observe such effects on deep, highly localized impurity states have not been successful since the critical concentrations for the MIT are beyond the impurity solubility limits [7].

Although the literature on the transport properties of doped semiconductors at and above the MIT is extensive, much less is known about electronic transport in the insulating region below the MIT for which thermally activated transport has been predicted [8,9]. In the limit of noninteracting impurities, the activation energy ε_2 equals the so called "Hubbard gap" U which corresponds to the energy difference between the neutral and the overcharged impurity state. At higher concentrations the gap is reduced by level broadening due to the interaction between adjacent impurity sites [1,9]. For shallow impurities with $1s$-like ground states, U is very close to the impurity binding energy E_B [10,11]. The gap can be seen only close to the MIT when it is reduced by interimpurity broadening [5,12,13]. Such broadening, however, reduces the impurity binding energy ε_1 as well. Consequently, whether charge transport occurs in the upper Hubbard impurity band or in the conduction (valence) band remains an open question [1,14,15]. Moreover, the significant contribution from hopping conduction with an activation energy ε_3 adds much complexity to the theoretical treatment of charge transport in this regime and makes a reliable determination of ε_2 rather difficult [13].

In this Letter we show that all these complications are eliminated in uniaxially stressed Ge:Cu. We find that the $2s$ states of the copper triple acceptors form Hubbard bands well separated from the valence band, providing a unique and simple model system to study phenomena associated with the evolution of impurity-related electronic states from a localized atomlike to extended metal-like character.

The samples in this study were prepared by copper diffusion into Ge single crystal wafers. Copper was Ar sputtered on the surfaces of Ge wafers that were individually sealed in quartz ampoules (under a vacuum or a helium atmosphere), annealed between 650 and 810 °C for 24 hours, and finally quenched in ethylene glycol. The concentration of copper acceptors is essentially controlled by the annealing temperature. With this procedure we have obtained samples with copper acceptor concentrations ranging from 3×10^{14} to 1.6×10^{16} cm^{-3}. The wafers were cut to produce a $1 \times 1 \times 5$ mm^3 final geometry for each sample. All resulting surfaces were $\langle 001 \rangle$ oriented.

Infrared spectroscopy, electrical resistivity, and Hall effect measurements were performed on the samples. The hole concentration as a function of temperature was obtained for a modified Hall-bar sample geometry with a magnetic induction of 3 kG [16]. Resistivity measurements were performed with the same system but without an applied magnetic induction. Uniaxial stress was applied parallel to the long axis of the bar-shaped samples using a leaf-spring/piston apparatus. A far infrared Fourier transform spectrometer was used to measure the low-temperature photoconductive response of the samples as a function of photon energy [17,18].

The temperature dependence of the resistivity for two Ge:Cu single crystals with and without stress is shown in Fig. 1. The magnitude of the applied stress is estimated from infrared spectroscopy measurements to be at least 4 kbar, i.e., the pressure above which the copper ground state transforms. Both samples were annealed at 700 °C; however, prior to the thermal treatment one crystal was n type with a shallow donor concentration of 4×10^{11} cm^{-3} (squares) while the other was p type with a Ga acceptor concentration of 3×10^{13} cm^{-3} (circles). At zero stress the resistivity of the sample with an n type background is increasing very rapidly with decreasing
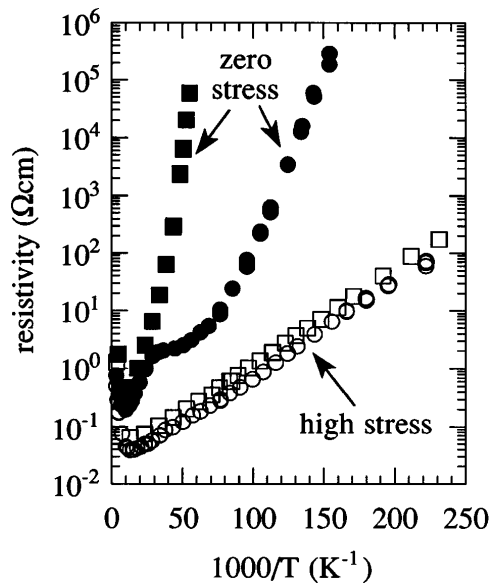
FIG. 1. Temperature dependence of the resistivity for two samples of different shallow dopant background and similar N_{Cu}. The squares and circles refer to samples 2 and 3 in Table I, respectively.

temperature due to the "freeze-out" of holes onto the 43 meV copper acceptor level. In the sample with p-type background doping, the initial freeze-out onto the copper level is followed by a freeze-out of holes onto the shallow acceptor level resulting in a lower resistivity at a given temperature.

Application of uniaxial stress produces a drastic decrease in the resistivity. Surprisingly we find that the high stress resistance is very similar for both samples, indicating that compensation effects and thus also hopping conduction do not play a prominent role in the electronic behavior observed for these samples down to liquid helium temperatures. Separate two point resistivity measurements have shown that the application of stress can produce a resistivity decrease by as much as 12 orders of magnitude at 4.2 K [17].

Figures 2(a) and 2(b) show the hole concentration and hole mobility, respectively, as functions of temperature

TABLE I. Dopant profile of samples. N_{Cu} is the substitutional copper concentration. The third column refers to the net shallow dopant concentration. In the case of sample 2, the shallow donor concentration is higher than that of shallow acceptors (indicated by the "−" sign). The fourth column shows the activation energy determined from the Hall-effect measurements at low temperatures ($T < 10$ K).

Sample	N_{Cu} (cm^{-3})	$(N_A - N_D)_{shallow}$ (cm^{-3})	Energy gap (meV)
1	3.0×10^{14}	2×10^{10}	3.7
2	3.0×10^{15}	-4×10^{11}	3.1
3	5.5×10^{15}	3×10^{13}	2.7
4	1.6×10^{16}	3×10^{13}	0

at high stress (>4 kbar) for samples whose parameters are listed in Table I. The hole concentration exhibits an Arrhenius behavior with an activation energy decreasing from 3.7 to 0 meV for the samples having Cu concentrations between 3×10^{14} and 1.6×10^{16} cm^{-3}. A remarkable feature of the data is that we could measure the hole concentration over a copper concentration range extending almost 2 orders of magnitude. This is possible because of the samples' high mobilities [Fig. 2(b)] characteristic of band rather than hopping conduction. In the past the onset of hopping conduction has severely limited the concentration range over which measurements of the Hall effect are possible. Consequently, in the analysis
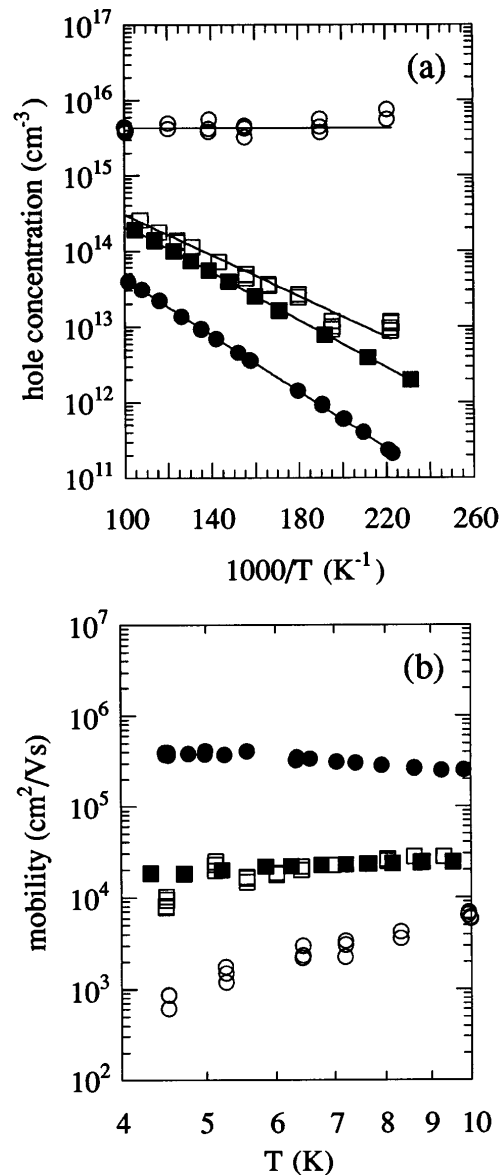

FIG. 2. Hole concentration and Hall mobility of uniaxially stressed samples. The filled circles and squares refer to samples 1 and 2, respectively, while the clear squares and circles refer to samples 3 and 4, respectively, as listed in Table I.

of activated transport below the MIT, one has relied on temperature dependent resistivity measurements and the assumption of a constant (i.e., temperature independent) mobility when determining ε_1, ε_2, and ε_3. However, such an assumption need not be valid.

In order to exclude the possibility that the zero gap observed in the heavily doped sample results from the merging of the impurity band with the valence band, we have measured the far infrared photoconductivity response in this sample. We find a response threshold at 16 meV which corresponds to the excitation from the Fermi energy in the impurity band to the valence band. Similar results have been previously reported for samples with a copper concentration of 3×10^{15} cm^{-3} [17,18]. Therefore, we conclude that the measured low-temperature electrical properties are entirely determined by hole transport within a copper-related impurity band that is well isolated from the valence band. Despite intense efforts such clear evidence for the existence of an isolated impurity band has never been found for semiconductors doped with shallow impurities [1,14,15].

Our results can be explained within the framework of impurity band conduction arising from the extended nature of the high-pressure $(1s)^2(2s)^1$ configuration of the copper acceptors. Uniaxial stress breaks the fourfold degeneracy of the valence-band edge and splits the acceptor lowest one-particle level into two, doubly degenerate levels. In the case of the copper triple acceptor, we have previously shown that at sufficiently high stresses (>4 kbar), the $2s$ one-particle level associated with the lower $1s$ split level crosses the higher energy $1s$ level transforming the copper ground state from a pseudo Li^0, $(1s)^3$-like to a normal Li^0, $(1s)^2(2s)^1$-like configuration having a stress insensitive first ionization potential [18]. Experimentally this ground-state transformation is manifested as a pressure-induced shift in the photoionization energy from a zero-stress value of 43.2 meV to a nearly constant value of 17 meV above 4 kbar.

The pressure-induced transformation is associated with a large redistribution of the hole density around Cu sites. The large highly localized density of the three holes on the $1s$ orbital is transformed into two still highly localized $1s$ holes and one much more delocalized hole on the $2s$ orbit.

At high stresses where Cu acceptors are in the normal Li-like $(1s)^2(2s)^1$ configuration, the radial dependence for the $2s$ wave function is that of a Li atom which is given by [19]

$$u_{2s}(r) = C\mu^{5/2}\left[r\exp\left(-\frac{\mu r}{a_B}\right) - \left(\frac{3A}{\mu}\right)\exp\left(-\frac{\mu b r}{a_B}\right)\right],$$
(1)

where a, b, and μ are the variation parameters, $A = (a+b)^3/(a+1)^4$, C is a normalization constant, and a_B is the hydrogenic Bohr radius. When a uniaxial stress of 4 kbar is applied along a $\langle 001 \rangle$ direction to a germanium single crystal, the Bohr radius a_B equals 6.4 nm and the

corresponding binding energy E_B is 7 meV [20]. It is evident from Eq. (1) that for a Li atom with $a = 4.03$, $b = 3.19$, and $\mu = 0.67$ the asymptotic behavior at large distances is governed by the first term in the square brackets. Using the wave function given by (1), we have calculated with Eq. (2) the Hubbard energy U, which is the energy required to place a second hole on the $2s$ state,

$$U = \int\int d\mathbf{r}_1 d\mathbf{r}_2 |u_{2s}(\mathbf{r}_1)|^2 \frac{e^2}{\varepsilon r_{12}} |u_{2s}(\mathbf{r}_2)|^2.$$
(2)

The integration yields $U = E_B F^0(2s, 2s)$ where $F^0(2s, 2s) = \mu D$ and D depends on the parameters a and b only [19].

The energy U represents the full Hubbard gap that should be observed at low concentrations when the overlap of the wave functions at adjacent sites is small. The overlap increases with increasing concentration resulting in a reduction of the gap [9]. To evaluate this effect the overlap energy I between wave functions located in impurity sites i and j separated by a distance R has been calculated using

$$I = \int d\mathbf{r} u_{2s}^i(\mathbf{r}) H u_{2s}^j(\mathbf{r}),$$
(3)

where H is the Hamiltonian for a hole interacting with sites i and j. The integration can be analytically performed by methods outlined in Ref. [21] and yields $I = \mu E_B S(w)$ where $w = \mu R/a_B$. for dilute systems with $w \gg 1$ the overlap function can be approximated by

$$S(w) = \frac{e^{-w}}{3}\left[\frac{11}{60}w^4 - \frac{w^3}{3} - w - 1\right].$$
(4)

Finally, the total broadening is obtained by a summation over all randomly distributed copper sites of concentration N_{Cu}

$$T = 4\pi N_{Cu} \mu E_B \left(\frac{a_B}{\mu}\right)^3 \int_0^\infty dw\, w^2 S(w).$$
(5)

In a simple approximation the energy gap Δ is given by $\Delta = U - T$. After substituting the numerical values for a and b into U and numerically integrating Eq. (5), we find that

$$\Delta = \mu E_B[0.49 - 352 N_{Cu}(a_B/\mu)^3].$$
(6)

The gap depends in a simple manner on the Cu concentration and on the parameter μ which is a measure of the extent of the hole wave function. For a perfect lithiumlike impurity having no central-cell correction ($\mu = 0.67$), the effective Bohr radius is $3a_B$, or 19.2 nm, and the binding energy equals $0.4E_B$, or 2.8 meV. The central-cell correction raises the binding energy to the experimentally observed value 17 meV [18] and is taken into account in our calculations by the adjustment of the parameter μ [22]. Whereas the binding energy depends strongly on the central cell, the terms U and T do not. Therefore by calculating Δ using Eq. (6), we can roughly

reproduce the concentration dependence of the energy gap with $\mu = 1.3$ (Fig. 3). The calculated U is about 16% higher than the experimentally observed gap at low N_{Cu}. This is not surprising, however, given the approximate nature of our calculation and since we have not included the electron-electron correlation effect in our calculations of U. In the case of hydrogenic impurities, this effect is known to reduce U by about 24% [11].

The data in Fig. 3 show that the gap Δ changes very little from 3.7 to 3.1 meV for the concentration change of 1 order of magnitude from 3×10^{14} to 3×10^{15} cm^{-3}. This clearly demonstrates that the full Hubbard gap U is observed in the low concentration sample. The result is qualitatively supported by our calculations from which one expects a practically constant gap Δ for N_{Cu} below 10^{14} cm^{-3}. Also it is important to note that as seen in Fig. 2(a), the low temperature hole concentration for the highly doped sample ($N_{Cu} = 1.6 \times 10^{16}$ cm^{-3}) is only about 4.5×10^{15} cm^{-3} indicating that for N_{Cu} just above the critical concentration only a partial overlap of the Hubbard bands takes place. Therefore, the observed critical concentration corresponds to a transition to a semimetallic rather than metallic phase.

One of the salient features of the presently studied system is that in a wide concentration and temperature range the conduction is governed by transport in a relatively deep impurity band without any interference from hopping or valence band conduction. This could provide a model system to study the correlation effects in a very low density gas of mobile holes. A number of effects including Wigner crystallization [2] have been predicted to occur at extremely low carrier densities and temperatures. We believe that Cu-doped Ge under uniaxial stress can satisfy these conditions and could be a promising medium for future studies of such effects.
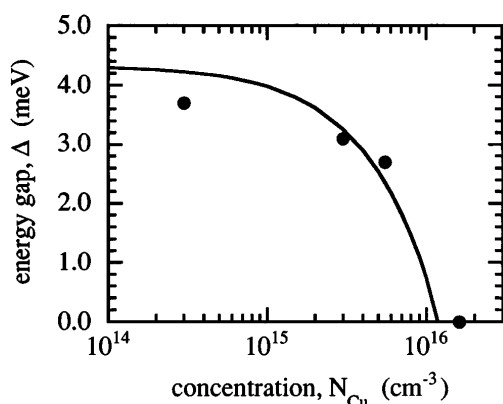
[1] N. F. Mott, *Metal-Insulator Transitions* (Taylor&Francis, London, 1990).
[2] D. Adler, in *Solid State Physics*, edited by Frederick Seitz, David Turnbull, and Henry Ehrenreich (Academic Press, New York, 1968), Vol. 21, p. 1.
[3] for an extensive review, see B. I. Shklovskii and A. L. Efros, in *Electronic Properties of Doped Semiconductors,* Solid State Series Vol. 45 (Springer-Verlag, Berlin, 1984).
[4] K. M. Itoh, E. E. Haller, J. W. Beeman, W. L. Hansen, J. Emes, L. A. Reichertz, E. Kreysa, T. Shutt, A. Cummings, W. Stockwell, B. Sadoulet, J. Muto, J. W. Farmer, and V. I. Ozhogin, Phys. Rev. Lett. **77**, 4058 (1996).
[5] X. Liu, A. Sidorenko, S. Wagner, P. Ziegler, and H. v. Löhneysen, Phys. Rev. Lett. **77**, 3395 (1996).
[6] T. F. Rosenbaum, K. Andres, G. A. Thomas, and R. N. Bhatt, Phys. Rev. Lett. **45**, 1723 (1980).
[7] B. V. Rollin and J. P. Russell, Proc. Phys. Soc. London **81**, 571 (1963).
[8] J. Hubbard, Proc. R. Soc. London A **276**, 238 (1963).
[9] J. Hubbard, Proc. R. Soc. London A **281**, 401 (1964).
[10] H. A. Bethe and E. E. Slapter, *Quantum Mechanics of One and Two Electron Atoms* (Academic Press, New York, 1957).
[11] H. Nishimura, Phys. Rev. **138**, A815 (1965).
[12] H. Fritzsche and M. Cuevas, Phys. Rev. **119**, 1238 (1960).
[13] E. A. Davis and W. Dale Compton, Phys. Rev. **140**, A2183 (1965).
[14] M. N. Alexander and D. F. Holcomb, Rev. Mod. Phys. **40**, 815 (1968).
[15] D. Jerome, C. Ryter, H. Schulz, and J. Friedel, Philos. Mag. B **52**, 403 (1985).
[16] O. D. Dubon, I. Wilke, J. W. Beeman, and E. E. Haller, Phys. Rev. B **51**, 7349 (1995).
[17] O. D. Dubon, W. Walukiewicz, J. W. Beeman, and E. E. Haller, in *Proceedings of the 23rd International Conference on the Physics of Semiconductors,* edited by Matthias Scheffler and Roland Zimmerman (World Scientific, Singapore, 1996), p. 2737.
[18] O. D. Dubon, J. W. Beeman, L. M. Falicov, H. D. Fuchs, E. E. Haller, and C. Wang, Phys. Rev. Lett. **72**, 2231 (1994).
[19] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960).
[20] R. Buczko and J. A. Chroboczek, Philos. Mag. B **50**, 429 (1984).
[21] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. 1.
[22] Y. Wu and L. M. Falicov, Phys. Rev. B **29**, 3671 (1984).

FIG. 3. Energy gap Δ versus substitutional copper concentration. The symbols represent the values determined from Hall-effect measurements (refer to Table I). The line refers to the energy gap computed by the method described in the text. Plotting Δ against the log of the copper concentration, one clearly sees the small change in Δ with decreasing concentration indicating the emergence of the full Hubbard gap.