

as we know, this is the first experiment which provides such a direct measure of the momentum dependence of  $s$ - $d$  exchange integral. Corresponding values for  $\xi_{\Delta}$  and  $\Delta$  from our data on Au-Fe are 33 Å and 0.25 eV, respectively; for Ag-Fe, 35 Å and 0.23 eV; and for Au-Mn, 36 Å and 0.23 eV.

Figure 4 shows some results for Cu-Fe, of particular interest because that system's  $T_K$  of approximately 21 K (Ref. 6) should put our measurements at 2 K in, or at least quite close to, the strong-coupling limit. Displayed is the resistance peak for 1.2 Å of Fe, 20 Å deep into the Cu compared with the undoped junction. The third curve is the symmetrized difference between the two divided by  $R_{UD}(V=0)$ . In contrast to Cu-Fe, Cu junctions made with Ni (no local moment) and Co ( $T_K \approx 10^3$  K) exhibit no sharp resistance peaks around zero.

Having no accepted theoretical scattering amplitude to which to compare the difference curve in Fig. 4, we point out instead some general features: (1) The half-width of the curve at half-maximum is about 1.6 mV corresponding to a temperature of 18.5 K, close to  $T_K \approx 21$  K. (2) A plot of  $\Delta R/R_0$  vs  $V^2$  (upper right) shows a squared dependence for  $V < 0.6$  mV which can be fitted to an expression of the form  $\Delta R(V) = R_0(1 - V^2/V_0^2)$  with  $V_0 = 1.66$  mV equivalent to 19.3 K. (3) Beyond  $V = 2.8$  mV the curve is linear on a semilog

plot. These observations for Cu-Fe, which are at least not inconsistent with the general picture which we have of the behavior of the many-body resonance, together with our evidence for the low- $T_K$  alloys presented earlier, give encouragement that this type of tunneling measurement can indeed provide us with a direct measure of the strong-coupling scattering amplitude for the Kondo problem.

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## Observation of an Electron-Hole Liquid in Cubic SiC

D. Bimberg and M. S. Skolnick

*Hochfeld-Magnetlabor des Max-Planck-Instituts für Festkörperforschung, 38042 Grenoble-Cedex, France*

and

W. J. Choyke

*Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235*

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The first observation of an electron-hole liquid (EHL) in the polar semiconductor cubic SiC is reported. The temperature and excitation dependence of the luminescence, time-delayed spectra and decay times ( $\tau_{EHL} = 57 \pm 3$  nsec) have been measured. An EHL binding energy of  $19.5 \pm 4$  meV, a high critical temperature of  $\sim 41$  K, and a low-temperature density of  $7.8 \times 10^{18}$  cm<sup>-3</sup> are deduced and demonstrate the strong influence of electron-phonon coupling and reduced screening for EHL binding.

Until recently Ge and Si were the only semiconductors which had been found to exhibit an electronic phase transition at low temperatures leading to the formation of an electron-hole liquid (EHL).<sup>1</sup> However, it has now been shown theo-

retically<sup>2</sup> that the electron-phonon interaction plays an important role in the stabilization of the EHL phase in polar materials. In this Letter we present evidence for the existence of an EHL in cubic SiC with a high critical temperature of  $\sim 41$

K. SiC has a strong electron- (hole-) phonon coupling. The electron-phonon-coupling constant  $\alpha$  is calculated to be 0.31, using a kinetic energy mass  $m_k = (m_i^2 m_l)^{1/3} = 0.33$ ,  $\epsilon_0 = 9.72$ , and  $\epsilon_\infty = 6.52^3$  as compared to an  $\alpha$  of 0.22 for GaP, where an EHL has recently been observed.<sup>4</sup>

SiC combines several other properties favorable for condensation into an EHL. The conduction-band minima are at point X. Thus the conduction band is anisotropic ( $m_l/m_t \approx 2.8$ )<sup>5</sup> with a valley degeneracy of three. In addition, SiC should have a highly anisotropic valence band at point  $\Gamma$ , as can be concluded from the extremely small spin-orbit splitting of the valence band.<sup>6</sup> All these factors lead to a reduction of the kinetic energy of the carriers. Finally, the exchange and correlation terms, which lead to EHL binding, are considerably less screened than in the elemental semiconductors.

The luminescence of pure *n*-type cubic SiC (residual impurity  $N$  at a level of  $\sim 10^{16} \text{ cm}^{-3}$ ) was excited by 2 nsec pulses from a 1-MW 337-nm  $\text{N}_2$  laser. Spectra with 488-nm  $\text{Ar}^+$ -laser excitation were also taken. The luminescence was detected with a fast photomultiplier and boxcar integrator. The time resolution of the system was  $\sim 10$  nsec. Figure 1(a) shows a series of spectra taken at 1.7 K and different excitation intensities. The luminescence spectrum  $\alpha$  [in Fig. 1(a)] was excited with the  $\text{Ar}^+$  laser. The A and B lines<sup>7</sup> of the exciton bound to a neutral nitrogen donor and their momentum-conserving (MC) phonon replicas [TA(X), LA(X), TO(X), and LO(X)] are clearly seen. These lines were recently identified by Dean *et al.*<sup>8</sup> as being the  $n=1$  and 2 components of a series of multiple bound excitons (MBE). The enhanced background between A and B may be due to unresolved MBE line structure.<sup>9</sup> The spectra  $\beta$  and  $\gamma$  [in Fig. 1(a)] were taken with the  $\text{N}_2$  laser. The excitation intensity increases from  $\beta$  to  $\gamma$  by a factor of 240. The MBE lines can still be clearly seen in spectrum  $\beta$ . A series of new lines, P-TA, P-LA, etc., appears in this spectrum; for clarity, only the P-TA replica is labeled. These lines grow first superlinearly with increasing excitation intensity, then merge to the band labeled EHL in Fig. 1(a) spectrum  $\gamma$ , which in turn increases linearly; at the same time, the MBE lines disappear. The EHL band is a superposition of the four MC phonon replica [TA(X) = 46.3 meV, LA(X) = 79.4 meV, TO(X) = 94.4 meV, and LO(X) = 102.8 meV].<sup>10</sup> A satellite of this band appears at  $\sim 100$  meV lower energy. This energy difference agrees well with

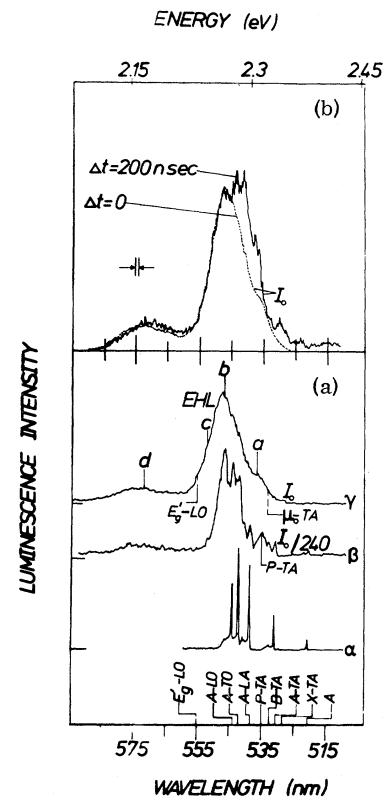


FIG. 1. (a) 1.7-K luminescence spectra of cubic SiC. The low-intensity spectrum  $\alpha$  was observed using  $\sim 100$  mW of the 488-nm line of an  $\text{Ar}^+$  laser and  $\beta$  and  $\gamma$  with a 1-MW  $\text{N}_2$  laser, with  $I(\gamma)/I(\beta) = 240$ . At the wavelengths  $a$ ,  $b$ ,  $c$ , and  $d$ , decay times were taken (Fig. 2). Below the spectra identifications of the lines are given. A(TA, LA, etc.) and B(TA, etc.) are replicas of  $n=1, 2$  states of the multiple bound excitons. X is the free exciton. P is a new high-excitation line out of which the EHL band grows at high excitation. The reduced gap is  $E_g'$  and the chemical potential is  $\mu_0$ . (b) Comparison of two normalized spectra, one undelayed [similar to spectrum  $\gamma$  in (a)] and the other delayed by 200 nsec. In the time-delayed spectrum long-lived impurity lines are visible.

the energy of the TO( $\Gamma$ ) and LO( $\Gamma$ ) phonons.<sup>10</sup> We shall concentrate here on the broad band at highest excitation intensities and demonstrate that it arises from an EHL.

Decay times were measured at four different wavelengths [ $a-d$  in Fig. 1(a) spectrum  $\gamma$ ]. The results are shown in Fig. 2. The decays are exponential with a time constant of  $57 \pm 3$  nsec for the wavelengths  $b-d$ , the small deviations being within the experimental uncertainty. The time constant at the high-energy side of the band (position  $a$ ) is a little but definitely longer, and is  $68.5 \pm 3$  nsec. The temperature dependence of the

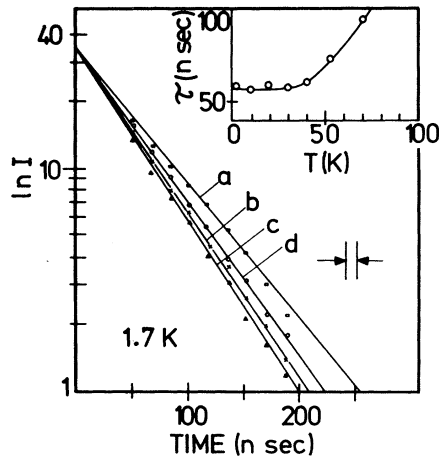


FIG. 2. Low-temperature time dependence of the luminescence at the wavelengths  $a$ ,  $b$ ,  $c$ , and  $d$  in Fig. 1 on a logarithmic scale. The gate width was 10 nsec and the spectrometer resolution  $6 \text{ \AA}$ . The vertical arrows indicate the time delays at which delayed spectra were taken.

decay time shown in the inset of Fig. 2 will be discussed later.

Time-delayed spectra give more complete information on the time dependence of the luminescence than decay times taken at particular wavelengths. Temperature-dependent time-delayed spectra were taken for delays  $t = 0, 80, 120,$  and  $200$  nsec relative to that of the luminescence maximum. Figure 1(b) shows a comparison between two spectra taken at zero delay and at a delay of  $200$  nsec, at  $1.7 \text{ K}$ . It is clear from these spectra that with increasing time delay the shape of the band which dominates the zero-delay spectrum does not change. However, as the decay times (Fig. 2) already suggested, at the high-energy side of the band long-lived bound-exciton lines reappear, which are undetectable in the undelayed spectra. These lines can be identified as the multiple-bound-exciton lines,<sup>8</sup> the decay time of the  $n = 1$  line being  $390$  nsec.<sup>7</sup>

The decay times, the time-delayed spectra, and the intensity dependence present clear evidence that the new high-excitation band EHL is due to the recombination of an electron-hole liquid with fixed reduced gap  $E_g'$  and Fermi energy  $E_F$ . The peak at  $\sim 5475 \text{ \AA}$  is due to the TO(X) MC phonon replica of the EHL recombination. The satellite peak at  $\sim 5730 \text{ \AA}$  can be attributed to two-phonon transitions of MC TO(X) or LO(X) phonons together with TO( $\Gamma$ ) or LO( $\Gamma$ ) phonons from the center of the Brillouin zone. Similar two phonon replica have also been observed in the lumines-

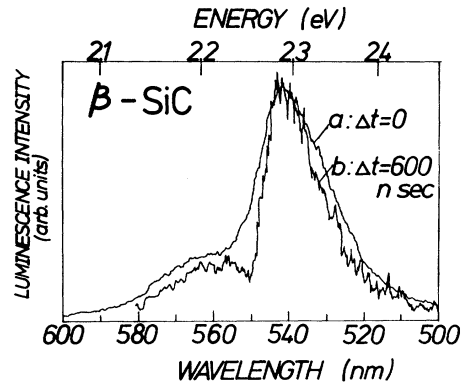


FIG. 3. Luminescence spectra taken at  $300 \text{ K}$ . (a) with the boxcar gate positioned for the maximum luminescence intensity at  $5420 \text{ \AA}$ , and (b)  $600$  nsec later.

cence spectra of bound excitons in cubic SiC.<sup>6,10</sup>

The recombination of an electron-hole plasma (i.e., gas) cannot explain the results presented here. The time-delayed spectra would show a narrowing of the luminescence line due to the increase of the reduced gap and the decrease of the Fermi energy with decreasing density as a function of time. This effect has been observed, e.g., in GaAs,<sup>11</sup> and also here in SiC at temperatures higher than  $T_c$ , the liquid-gas phase-transition temperature. Figure 3 shows two spectra taken at  $300 \text{ K}$ . The time delay of spectrum  $b$  is  $600$  nsec relative to that for spectrum  $a$ . The decreased width and shift to higher energy of the delayed spectrum is characteristic of an EH plasma as opposed to the EHL in Fig. 1(b). A lower limit for the critical temperature  $T_c$  ( $\geq 41 \text{ K}$ ) can be determined in three ways: (1) The undelayed luminescence line shown in Fig. 1 remains at the same energy up to  $41 \text{ K}$ , where it starts to shift strongly to *higher* energies (the band gap shifts to *lower* energy by only  $1 \text{ meV}$  between  $2$  and  $77 \text{ K}$ ).<sup>8</sup> (2) The decay time of the peak  $b$  in Fig. 1(b), spectrum  $\gamma$ , remains constant up to  $41 \text{ K}$ —which also indicates, of course, that some sample heating occurs—and then increases strongly towards higher temperatures, as shown in the inset of Fig. 2. (3) The delayed and undelayed spectra are identical up to  $41 \text{ K}$  (apart from the impurity-related features which appear at lower temperatures). At temperatures higher than  $50 \text{ K}$ , typical plasma behavior is observed. The actual value of  $T_c$  is not expected to be much higher than  $41 \text{ K}$ , since at  $50 \text{ K}$  no EHL-like behavior is observed for any excitation intensity.

The energy of the reduced gap  $E_g'$ (LO) of the

EHL can be determined from the low-energy tail of the main band in spectrum  $\gamma$  in Fig. 1(a) to be  $2.235 \pm 0.004$  eV. The position of the Fermi energy of the TA replica is  $2.323 \pm 0.004$  eV. This energy can be used to calculate the energy difference between the EHL ground state and the known energy position of the free exciton<sup>6</sup> (the work function of the EHL) to be  $19 \pm 4$  meV. A value of 13.5 meV has been estimated for  $E_x$  from absorption experiments.<sup>7</sup> However, this value was derived indirectly and might be too low. A theoretical calculation gives  $E_x \approx 20$  meV.<sup>12</sup> With use of this theoretical value, the ground-state energy is obtained as  $(19 \pm 4) + 20$  meV =  $39 \pm 4$  meV. Assuming that the intensity ratios of the MC phonons of the EHL band in Fig. 1(a) spectrum  $\gamma$ , are the same as those of the bound excitons, one gets  $I(\text{TA}(X)):I(\text{LA}(X)):I(\text{TO}(X)):I(\text{LO}(X)) = 1:2.44:3.0:1.5$ , in agreement with corresponding values we have obtained for the free-exciton phonon replicas. With these ratios and a Fermi energy of  $32 \pm 4$  meV, the observed line shape is described well.

The density of the EHL can now be estimated. The Fermi energy of the electrons and holes is

$$E_F = \sum_{a=1}^2 \frac{\hbar^2}{2m_a \nu_a^{2/3}} \left( \frac{3\pi^2 n}{1 + \Gamma_a^{3/2}} \right)^{2/3},$$

with  $m_1 = (m_t^2 m_l)^{1/3}$ ,  $\Gamma_1 = 0$ , and the number of valleys  $\nu_1 = 3$  for the electrons and  $m_2 = m_{hh}$ ,  $\Gamma_2 = m_{lh}/m_{hh}$ ,  $\nu_2 = 1$  for the holes. Here  $m_t = 0.24m_0$  is the transverse electron mass,<sup>5</sup>  $m_l = 0.647m_0$  the longitudinal electron mass,<sup>5</sup>  $m_{hh}$  the heavy-hole mass, and  $m_{lh}$  the light-hole mass. From an interpolation of the Si and C valence band values given by Lawaetz<sup>13</sup> one gets  $\gamma_1 = 4.4$ ,  $\gamma_2 = 0.37$ ,  $\gamma_3 = 1.37$ ,  $m_{lh} = 0.125m_0$ , and  $m_{hh} = 1.2m_0$ . The uncertainty of  $\gamma_2$  and  $\gamma_3$  is not too important (the anisotropy could be higher), since  $\gamma_1$  should be correct to within 10% and the hole Fermi energy is smaller than the electron Fermi energy. Using the above values a density of  $\sim 7.8 \times 10^{18} \text{ cm}^{-3}$  is obtained, which is 2.6 times larger than in Si. The ratio  $T_c/n^{1/2} = 15 \times 10^{-9} \text{ K cm}^{3/2}$  is in excellent agreement with the low-temperature ratio for Si,  $16 \times 10^{-9} \text{ K cm}^{3/2}$ , as predicted by the universal scaling law given, e.g., by Hensel, Phillips, and Thomas.<sup>1</sup>

The high density and binding energy which are more than twice those found in Si with its similar effective masses, but larger electron-mass anisotropy and a valley degeneracy of 6, demonstrate the great importance of the reduced screening of the Coulomb interactions and of electron-

phonon coupling for the stabilization of the EHL in SiC and related polar materials. The existence of multiple bound excitons, an electron-hole plasma, and an electron-hole liquid in the same material provides fertile ground for the study of the successive evolution of these phenomena in the visible part of the spectrum. In addition, we have recently obtained evidence for the EHL in hexagonal 2H-SiC, a polytype with a band gap 1 eV larger than cubic SiC. It will be of considerable interest to study the change in the EHL properties as a function of the change of band structure through the range of polytypes between these two extremes.

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<sup>9</sup>A careful evaluation of the spectra of type  $\alpha$  in Fig. 1(a) shows the presence of a weak line at  $\sim 5475 \text{ \AA}$ , the wavelength at which the EHL-TO line grows. Independently P. J. Dean has obtained evidence for the presence of similar spectral features at this excitation intensity.

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## Intermolecular Relaxation Energies in Anthracene

W. R. Salaneck

Xerox Webster Research Center, Webster, New York 14580

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A type of angle-dependent uv photoemission measurement has been used to study variations in the intermolecular polarization effect at the surface of thin condensed anthracene films. The top molecular layer exhibits a 1.2-eV relaxation energy in response to the polarization of the hole state created in photoemission event. The second and subsequent layers exhibit a different value of about 1.5 eV. This result corresponds to the observation of a surface electronic molecular-ion state on a molecular solid.

The purpose of this Letter is to report the first observation of a surface electronic molecular-ion state energy different from that of bulk molecules in a molecular solid. The study employed condensed anthracene films, and a type of angle-dependent ultraviolet photoemission spectroscopy (UPS). The surface molecules exhibit hole-state binding energies less than from those in the succeeding layers, corresponding to a surface intermolecular relaxation energy which is less than that in the bulk molecular solid.

A true molecular solid is one in which only weak van der Waals forces hold the molecules together in the solid. The electronic structure of the individual molecules in the solid phase is essentially unchanged from that in the vapor phase, the electronic structural features of the molecular solid being determined by those of the independent constituent molecules. When an electron is photoemitted from a molecule in the vapor (*v*) phase, the remaining electrons relax in response to the hole state created. This *intramolecular* polarization results in some so-called relaxation energy being given to the escaping electron, increasing its kinetic energy, decreasing its apparent binding energy, and leading to shakeup satellite peaks<sup>1</sup> on the low-kinetic-energy side of primary peaks in UPS and x-ray photoemission spectroscopy (XPS). In the condensed or solid (*s*) phase, there exists an additional *intermolecular* relaxation energy, due to the polarization of other electrons in neighboring molecules.<sup>2</sup> This latter case has been cast in a dielectric formalism,<sup>3</sup> ignoring surface effects.

In the UPS measurement, the *intermolecular* polarization effects shifts the UPS(*s*) hole-state

spectrum rigidly toward higher kinetic energies (lower binding energies) with respect to the corresponding UPS(*v*) spectrum. The amount of the rigid shift,  $\Delta_r$ , is equal to an intermolecular relaxation energy.<sup>4-6</sup> Obviously, a molecule in the top monolayer of a molecular solid will experience a dielectric environment (essentially a dielectric half-space) different from that of a molecule within the bulk. This phenomena was predicted by Duke *et al.* in an analysis of electronic localization phenomena and the apparent broadening of UPS spectra of polymers and other molecular solids.<sup>4,7</sup> Until this present work, however, no direct experimental observation of surface molecular-ion states on molecular solids existed.

Anthracene was chosen as an ideal molecule with which to look for a depth-dependent  $\Delta_r$  for several reasons: (a) Its first  $I_p$  (photoemission peak) corresponds to a delocalized  $\pi$  state,<sup>8</sup> well separated at lower binding energy from the remaining  $I_p$ 's<sup>9</sup>; (b) the molecule is large, flat, thin, and stable, enabling the preparation of thin vapor-deposited films to be formed, which under the proper conditions will have the molecules lying flat on the substrate<sup>10</sup>; and (c) optical studies of surface excitons have shown them to be slightly different than those in the bulk.<sup>11</sup> The hole state of the present work, however, is qualitatively and quantitatively different than the exciton state.

The experiments were carried out at  $10^{-9}$  Torr in an AEI ES 200B photoelectron spectrometer, which employs a hemispherical electron-kinetic-energy analyzer with slit filtering, resulting in about a  $4^\circ$  angular acceptance of photoemitted