Evidence for a hard gap and Wigner lattice in heavily boron-doped synthetic diamond

Tomoko Sudou,[1,*] Kazutoshi Ohashi,[1,†] Toshimaro Sato,[2] Eiji Ohta,[2] Satoru Okayasu,[3] and Hiroyuki Sugai[3]
[1]*Faculty of Engineering, Tamagawa University, Tamagawagakuen 6-1-1, Machida, Tokyo 194-8610, Japan*
[2]*Graduate School of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 228-8522, Japan*
[3]*Department of Material Science and Engineering, Japan Atomic Energy Research Institute (JAERI), Tokai-mura, Naka-gun, Ibaraki 319-1106, Japan*
(Received 14 May 2004; published 21 January 2005)

We have measured low frequency generation-recombination noise (g-r noise) spectra of a heavily boron-doped diamond crystal over the temperature range 20–300 K. The experimental results show that there are two peaks in the g-r noise spectrum at 120 K and 67 K, respectively. The 120 K peak corresponds to experimental evidence for existence of a hard gap having width of 10.4 meV. We interpret the 67 K peak as evidence for Wigner lattice formation whose gap width is 5.8 meV.

DOI: 10.1103/PhysRevB.71.045211 PACS number(s): 72.80.−r, 71.55.−i, 72.70.+m, 81.30.−t

I. INTRODUCTION

Theoretical investigations of low-temperature hopping conductivity in a Coulomb-correlated localized semiconductor are still controversial among researchers. The central question is whether elementary charge excitations are due to ordinary single particles or large many-body composite particles. Mott[1] proposed the variable-range hopping (VRH) theory which is based on one-electron hopping processes. Efros and Shklovskii[2] modified Mott's argument to include the effects of long-range Hartree interactions between single-particle excitations and predicted the soft Coulomb gap in the single-particle density of states near the Fermi energy E_F. On the other hand, the applicability of Mott's and Efros's theories to Coulomb glass has been controversial because these theories neglect many-electron effects, in particular the correlated motion of electrons. The importance of many-electron effects was pointed out by Pollak[3] as early as 1970. This effect is due to the existence of a relatively large density of compact low-energy electron-hole pair excitations. Such compact electron-hole pair excitations arise because a transfer of an electron changes the energy of electrons at nearby sites and thus affects transitions of other electrons. The separated electron-hole pair generates electric dipole moments. This polarization releases a relaxation energy which lowers the total energy of excitation and then induces the hard gap.[4,5] Consequently, the density of states shows exponential functional dependence, so that within the hard gap the density of states is effectively zero over a finite range of energy. The manifestation of the hard gap is that upon lowering temperature the conductivity σ as a function of temperature T shows a crossover from the form given by VRH to an activated form $\sigma \propto \exp-(\Delta/k_BT)$ associated with transition of carriers across the hard gap, where Δ is the hard gap width and k_B is the Boltzmann constant.

From an experimental point of view, the observed temperature dependence of the conductivity can be described in a sufficiently accurate way by the one-electron theory of Efros and Shklovskii. However, at very low temperatures, the Arrehenius law of conductivity has been observed experimentally. For examples, a crossover from VRH conduction to Arrehenius form conduction with decreasing temperature has been found in $Cd_{0.91}Mn_{0.09}Te:In$,[6] ion-implanted Si:P,B,[7] ion-implanted Si:As[8] and insulating Si:B[9] samples. In the insulating Si:B[9] sample, the hard gap width Δ is about 0.03 meV, so that it is impossible to observe conductivity of the activated form for temperatures above 1 K. In our previous paper,[10] we have performed measurements of conductivity of a highly boron-doped semiconducting diamond which exhibits the Mott VRH, the Efros VRH and the crossover from VRH law to activated Arrehenius behavior in the liquid nitrogen temperature region. Due to the high energy level of the boron acceptor, i.e., $E_A = 0.35$ eV above the valence band, conduction in the valence band becomes negligible at relatively high temperatures. Furthermore, the high energy level of the acceptor level makes it possible to dope boron impurity in concentration as high as 100 ppm, so that the hard gap having a large width of about 11 meV can be induced. We observed the crossover from VRH conduction to simply activated Arrehenius conduction with decreasing temperature around 50 K, which showed the existence of a rigid hard gap in doped diamond.

Tenelsen *et al.*[11] and Perez-Carrido *et al.*[12] investigated low-temperature conductivity in Coulomb glass by computer simulation and found that low-temperature conductivity would be strongly influenced by many-electron hopping processes. In other words, the hop of an electron affects hopping probability of other electrons. In addition to such sequential correlation, long-range interaction produces the possibility of collective hopping of several electrons in transition. Hence, it is certain that hopping creates the possibility for rearrangements of many electrons among random impurity sites. Such stochastic fluctuation of the carrier configuration should bring about fluctuation of hopping conductivity which is proportional to the number of electrons in the current path. Theoretically, Shklovskii *et al.*[13] suggested that the low-frequency $1/f$ noise for hopping conduction was due to fluctuations of the number of carriers belonging to the current path. These fluctuations are caused by slow exchange of electrons between the current path and other donors in the interstices. On the other hand, Kogan[14] has suggested that the $1/f$ noise in the interacting VRH system can arise from stochastic fluctuations among low-energy many-electron

configurations. Experimentally, Lee and Massey[15] have presented low-frequency noise spectoroscopy in nonmetallic *p*-type Si:B crystals in the region of VRH conduction at low temperatures. Their low-frequency noise spectra suggest that many-electron processes are important to charge dynamics in the interacting regime.

In semiconductor materials, low-frequency noise is usually composed of $1/f$ noise and generation-recombination noise (g-r noise) of local levels. The g-r process is caused by fluctuation of electronic transition rates between localized trap levels in the forbidden gap and the conduction or valence bands. These number fluctuations of conducting charge carriers may cause the Lorentzian shaped g-r noise contributions in the spectrum. Several authors[16–18] have measured g-r noise of discrete impurity level systems as a function of temperature and have estimated the energy position in the forbidden band. In the case of our diamond specimen the hard gap width is so narrow that carriers can be easily transferred across the hard gap with help of thermal energy. When temperature is increased from a low temperature, the maximum of noise spectrum occurs at the temperature of $T=\Delta/k_B$ because the number of generated carriers and recombining carriers are large at this temperature. For temperatures of $T>\Delta/k_B$, the corresponding noise amplitude decreases because the g-r process disappears. By using this experimental method in which excited carriers can be created by heating instead of illumination, we should be able to detect the hard gap.

Boron concentration contained in our specimen is about 100 ppm. The boron concentration per unit volume of the specimen is equal to $n_B=1.76\times10^{19}/\mathrm{cm}^3$. The mean distance between a boron impurity and its nearest neighbor, that is the mean distance between holes, is given by 23.8 Å. We can estimate the effective Bohr radius from $a_B=a_0[\kappa/(m^*/m_0)]$ where a_o is Bohr radius for hydrogen. Using effective mass $m^*=1.1m_0$ (Ref. 19) for a hole, where m_0 is free electron rest mass, and relative dielectric constant in diamond $\kappa=5.66$, we find $a_B=2.72$ Å. The effective Wigner–Seitz distance becomes $r_s=8.75$. In high carrier concentration, the zero-point energy arising from the Pauli exclusion principle dominates, resulting in a liquid state. As density is reduced, Coulomb interaction in the medium becomes important, ultimately ordering the carriers into a crystal. It is now generally accepted that the electronic assembly will crystallize out at sufficiently low densities. This idea is due to Wigner,[20] and the crystallizing electron lattice structure is termed the "Wigner lattice." The argument for Wigner lattice formation and the conditions under which it is expected to occur are elaborated on in various directions. Many authors estimated the critical Wigner–Seitz distance r_s at which the Wigner transition is expected to occur at 0 K. For review and reference, see the paper by Care and March.[21] Ceperly[22] performed Monte Carlo numerical simulations for the ground state of an electron system and predicted that at zero temperature the Wigner phase transition from liquid to solid occurs at $r_s\approx67-100$ for a three-dimensional (3D) system. Apparently this large critical distance $r_s\approx100$ has made the observation of 3D Wigner crystallization (WC) phenomena difficult. The major obstacle is the tendency toward disorder-induced electron localization at densities much higher than those associated with Wigner crystallization.

Tanatar and Ceperley[23] found from their Monte Carlo simulation that the critical density, expressed in terms of the Wigner–Seitz distance r_s, is $r_s=37$ for ideally clean two-dimensional electron (2DE) systems. Disorder, which is always present in any experimental system, plays an important role. Chui and Tanatar[24] found from their Monte Carlo studies that the disorder introduced in their model could stabilize the WC phase at r_s as low as 7.5. From an experimental point of view, Yoon *et al.*[25] reported transport studies in the large r_s regime of 2D hole systems in the semiconductor heterostructures. They found that the metal-insulator transition (MIT) in zero magnetic field in clean 2D heterostructures occurred at $r_s=35.1$. They also examined the dependence of r_s at MIT on the disorder in the sample. The r_s, at which the 2D MIT is observed, depends strongly on the disorder in 2D system. In the inset of Fig. 1 of Ref. 25, they plotted the 2D MIT critical r_s as a function of scattering rate of the 2D carriers. The critical r_s for WC for a impure 2D system is in agreement with the critical r_s predicted by Chui *et al.* In our boron-doped diamond, there are many acceptor centers. If a hole is trapped by an acceptor center, its repulsive interaction with neighboring holes will be reduced by the acceptor potential. The untrapped holes will rearrange themselves to form a local Wigner lattice with a hole density higher than that of the clean system. Hence, we can expect that WC phase may be stabilized at a smaller value of r_s in doped diamond. Furthermore, Mott[26] considered a 3D electron system at zero magnetic field and found the critical value $r_s=20$ from a comparison of energies of WC lattice state and metallic state, and estimated the Wigner gap width to be about one hundredth of the potential energy between carriers. The potential energy of our diamond is approximately $V=107$ meV, so that the Wigner gap width is estimated to be $\Delta_{\text{Wigner-gap}}=V/100=1.07$ meV. In this paper, we will present experimental evidence for a collective hole solid at zero magnetic field in a 3D boron-doped diamond crystal.

II. EXPERIMENTAL METHOD

The sample used in these noise studies is a boron-doped synthesis diamond grown by Sumitomo Denko Co. Ltd. The crystal size is $3.0\times3.0\times0.3\ \mathrm{mm}^3$ with plane surface of (100) crystallographic planes. Our diamond sample contains a boron, whose concentration is about 100 ppm. We measured the low-frequency noise ($f=1-100$ Hz) using the five-point bridge configuration described by Scofield.[27] This method can give a large rejection of all common-mode fluctuations including temperature and current by sending a balanced current through two identical halves of the sample and measuring only the difference signal. A block diagram of our measurement system is shown in Fig. 1.[28] For this measurement, the sample current was biased by a 6 V Li Gell cell battery hooked in series with wire-wound resistors soldered in for controlling the current. The voltage leads of the specimen were connected to a PAR 1900 transformer across the 10:1000 terminals for a gain in the transformer of 40 dB. The input of the transformer also had a blocking capacitor of 25 000 pF at the front end to prevent dc current from affecting the transformer. The output of the transformer was dc

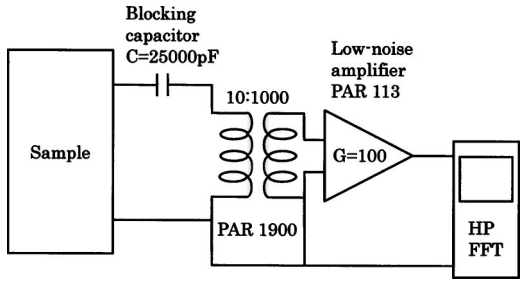

FIG. 1. A block scheme of experimental arrangement for noise measurements.

coupled to a PAR 113 low-noise amplifier with its gain set to 100, yielding another 40 dB. This gain gave the amplifier system a total gain of 80 dB. The output of the amplifier was fed into HP FFT system where the data was captured and analyzed. The specimen was fixed by the use of a holder. The holder was placed in a liquid-helium cryostat in temperature range from 20 to 300 K. Throughout the experiment, temperatures of the diamond were measured by using AuFe-Chromel thermocouple.

Three electric contacts, consisting of 1.0 mm diameter, were arranged on the surface of the diamond. We took care to achieve ohmic contacts, because contacts present an additional possible source of error. At first the sample was degreased for 10 min by ultrasonic vibration in trichloroethylene and then ultrasonically rinsed in acetone. The sample was then rinsed under a stream of 18 MΩ cm deionized (DI) H_2O and dried with high-purity nitrogen. The sample was inserted into a deposition chamber after the drying process. Ac magnetron sputtering of the contacts could be done in the same apparatus. The ohmic contacts were made to the diamond by depositing In–Ag(25%,75%) by ac magnetron sputter deposition at a power of 100 W. The pressure in the vacuum system was better than 1×10^{-6} Torr. Argon gas (99.999%) was admitted up to a pressure of 2×10^{-3} Torr. The thickness of the contacts is 5000 Å. Figure 2 shows the $I-V$ characteristic of the sample between two contact dots at

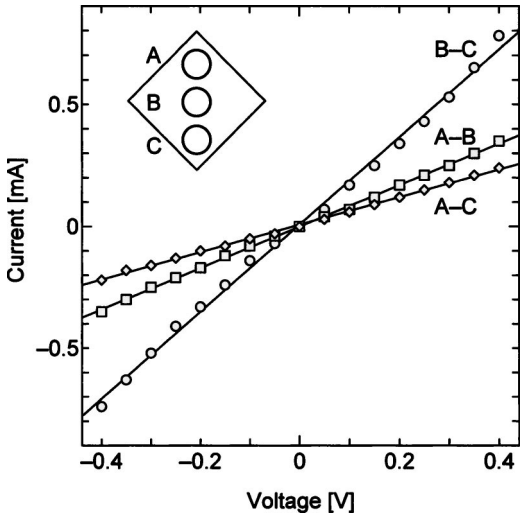

FIG. 2. Current-voltage characteristics of sample between two contact dots of 1 mm diameter at room temperature.

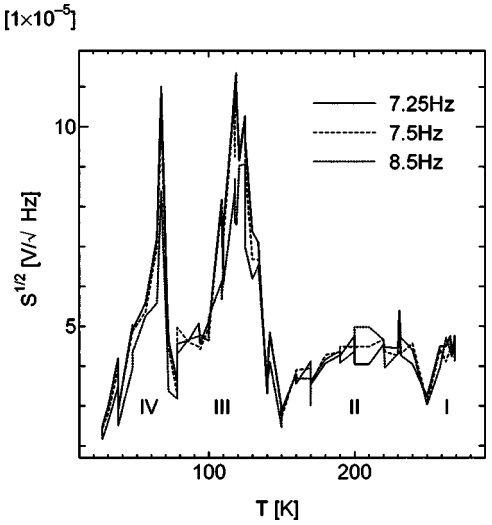

FIG. 3. The square root of the noise spectral density $S^{1/2}$ of boron-doped diamond as a function of temperature for three different frequencies, i.e., 7.25, 7.5, and 8.5 Hz.

room temperature. The contacts have clearly become ohmic. The resistance R_{AB} of the diamond between A and B contacts is 1174.1 Ω. The resistance between B and C contacts is $R_{BC}=556.6$ Ω and that between A and C contacts is $R_{AC}=1768.5$ Ω.

III. RESULTS AND DISCUSSIONS

The low-frequency voltage noise measurements were carried out in temperature range 20–300 K at frequencies of 1–100 Hz. Figure 3 shows the temperature dependence of the square root of the noise spectral density $\sqrt{S_V(T)}$ measured at 7.25, 7.5 and 8.5 Hz, respectively. The noise amplitude as a function of temperature $\sqrt{S_V(T)}$ shows two peaks at 67 K and 120 K. These noise peaks are observed almost at the same temperature for different frequencies. Here, it is convenient to divide the noise characteristics into four regimes as shown in Fig. 3. Region I (above 250 K) corresponds to thermally activated conduction of holes. These holes are activated from the boron impurity level into the valence band as demonstrated by Massarani *et al.*[29] who measured the electric conductivity of synthetic boron-doped diamonds in the temperature range 12–300 K. They observed that the slope of conductivity against the inverse of temperature, $\ln\sigma$ vs. T^{-1}, changed abruptly in the range above 200 K and considered this abrupt change due to transition from a conduction in the valence band to a hopping regime. The generation-recombination process (g-r noise) can be described by a random process with a time constant τ. From the Fourier analysis of this random process, we obtain the expression for the Debye–Lorentzian noise spectrum of $S(f)\approx F(1-F)\tau/[1+(2\pi f\tau)^2]$, where F is the equilibrium state occupancy given by $F=1/\{1+\exp[(E-E_F)/k_BT]\}$. In the case of wide gap semiconducting diamond, fluctuations are expected to occur very slowly, so that the time constant τ is large. We observed the noise power form of $1/f^2$ in our diamond specimen above 1 Hz at room temperature. For

wide gap semiconductors, such as GaAs and SiC, the $1/f^{\alpha}$ noise[30] was observed where α lies in the range 1.3 to 1.5.

In region II (150–250 K), we have observed that the amplitude of noise is only weakly dependent on temperature above 180 K, but decreases with temperature below 180 K. The frequency dependence of the noise power spectra follows the $1/f$ law. Region II is the Mott VRH region as shown clearly by the temperature dependence of the resistivity of the specimen (see Fig. 3 in Ref. 10). A similar behavior of the low-frequency noise spectra was reported by Shlimak *et al.*[31] on doped Ge, and Lee *et al.*[15] on doped Si:B crystals. Shlimak *et al.* measured the low-frequency ($f=0.1-50$ Hz) current noise in samples of *p*-type Ge:Ga and *n*-type Ge:As at temperatures of 1.3–4.2 K. The spectral density of noise has a $1/f$-form. The temperature dependence of the noise is much weaker. The origin of such weak temperature dependence was explained by Shlimak *et al.* who suggested that the noise might be related to mobility fluctuations, that is hopping probability fluctuations, rather than to carrier number fluctuations as suggested by Shklovskii.[13] The mobility fluctuations are assumed to be due to fluctuations of hopping site energies produced by charge redistribution in the surroundings. Both hopping site energy fluctuations and temperatures influence the fluctuations of resistance. These two effects tend to cancel each other out, leading to the weak temperature dependence of noise intensity. Lee *et al.* also measured the low-frequency ($f=0.1-12$ Hz) noise spectra in boron-doped silicon crystals in temperature range 1.5–7 K. Their noise data show that the amplitude is weakly dependent on temperature above 2 K but decreases below 2 K. They pointed out that the temperature dependence of noise spectra below 2 K could not be resolved with existing models of single-particle hopping fluctuations by Shklovskii and Kogan,[13] and by Kozub.[32] However, they concluded that the noise data were qualitatively consistent with the thermally activated fluctuation model of Dutta, Dimon and Horn.[33] An overall temperature dependence of noise spectra observed in region II of our diamond sample is similar to the behavior for doped Si crystal at low temperatures as described above. Considering the ratio of the hard gap of diamond to silicon given by $\Delta_{\text{hard-gap}}(\text{diamond})/\Delta_{\text{hard-gap}}(\text{silicon}) \approx 11/0.03 \approx 300$, it is expected that the same phenomenon that happened in silicon should occur in diamond at a higher temperature by two orders of magnitude. We speculate that the decrease in noise amplitude of doped diamond below 180 K in region II is caused by the decrease of number of carriers because there is the decrease of state density due to the appearance of the soft Coulomb gap. Then the observed tendency that $S_V(T)$ remains nearly constant above 180 K in the region II can be explained by the assumption that carrier concentration remains nearly constant in this region of the temperature. At temperatures corresponding to the hopping conduction region (region II), the frequency dependence of noise power spectrum $S_V(f)$ follows the $1/f$-law. This result shows that in the hopping region there should exist long relaxation times. Relaxation times of low-lying excited states of electron glass have been studied by Mochena *et al.*[34,35] They found some extremely slow relaxation processes and associated them with relaxation from meta-stable states to the ground state of electron glass.

In region III (75–150 K) of Fig. 3, we observed a peak of noise power density at 120 K. This region is identified as the Efros VRH region from the measurements of resistivity. The Lorentzian type of noise power density can be ascribed to fluctuations in the number of free carriers which is equal to the number of occupied excited states. The Lorentzian noise power is proportional to the factor $F(1-F)$, where F is the equilibrium state occupancy. This factor is a sharply peaked function of energy around E_F with a line width of the order of k_BT. We consider the two-level system, which arises from disorder, to approximate our situation with the hard gap. The upper level is the excited state and the lower is the ground state. When the thermal energy is smaller than the hard gap width, $T<\Delta/k_B$, the magnitude of the g-r noise is small because the transition probability is small. On the other hand, when $T>\Delta/k_B$, the carrier can be transferred easily to the excited state with the help of thermal energy. The magnitude of noise again becomes small because the g-r process disappears. Carrier number fluctuations will become maximum when $T=\Delta/k_B$, so that the maximum of $S_V(T)$ is expected to occur at this temperature. From this method, we can estimate the hard gap width. We consider that the observed peak at 120 K corresponds to the situation where the generation and recombination of carriers across the hard gap becomes maximum. Then, the hard gap width causing the noise peak at $T=120$ K is given by $\Delta=120k_B=10.4$ meV. The value obtained in this way is in good agreement with the hard gap width $\Delta=11$ meV obtained from the conductivity $\sigma(T)$ measurement.[10] Hence, we prove the existence of the hard gap in a highly boron-doped diamond by using the noise measurements.

Many papers[36–39] present the studies of the effect of temperature-induced smearing of the Coulomb gap which was predicted theoretically. At low temperatures, there is a deep minimum in the density of states but its depth is decreased as temperature is raised, and for $T>0.3$ it disappears. Here, the value of k_BT is given in the units of $e^2n^{1/3}/\kappa$, n being the concentration of carriers. In the case of our specimen, $T=0.3$ corresponds to 372 K. Our previous paper[10] shows that below 50 K the single activated conduction due to the hard gap is observed. More definite information about the hard gap has been obtained by measuring the absorption coefficient of boron-doped diamond at room temperature. The observed optical gap width is equal to the value of the electrical transport result. These experimental results show that the hard gap does not vanish completely up to room temperature.

Next, we will discuss our experimental results in region IV. We detected a noise peak(IV) at $T=67$ K in our sample. According to the above arguments, this peak corresponds to the energy gap, whose width is $\Delta_{Wigner\text{-}gap}=67k_B=5.8$ meV. Furthermore, large fluctuations in the noise spectrum are observed around 25 Hz. This appearance of eigenfrequency modes suggests that the correlated motion of carriers occurs in the sample. According to Wigner, who used a semiclassical approach, the ground state of the jellium model has a bcc lattice structure at sufficiently low densities. The quantum mechanical approach was developd by van Dijk and Vertogen[40] using quantum field techniques. According to the theoretical results of van Dijk and Vertogen, the energy dif-

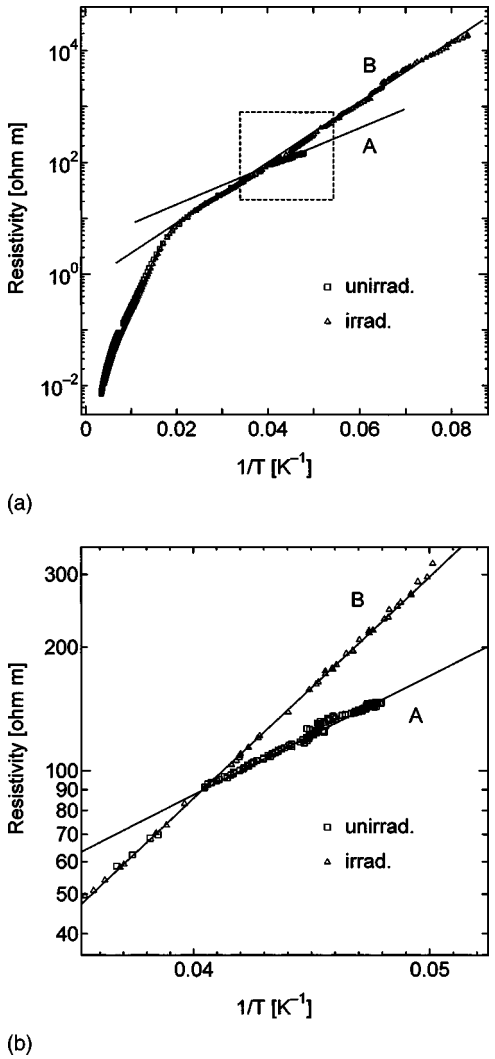

FIG. 4. (a) Resistivity $\ln \rho$ versus T^{-1}: unirrad., before the irradiation; irrad., after the irradiation of 3.80×10^{14} ions/cm^2 phosphorus implantation dose. The data has been fit with simple activation conduction (lines A and B). The box shows the extent of (b). (b) Resistivity $\ln \rho$ versus T^{-1}. The full lines A and B represent simple activation conduction.

ference per electron between the Hartree–Fock energy of Wigner lattice and that of the free electron gas is estimated to be $\varepsilon=-1.3\times10^{-2}$ Ryd for Wigner–Seitz distance $r_s=8.75$. We can estimate the effective Rydberg to be Ryd $=0.467$ eV from the relation Ryd$=$Ryo$[(m^*/m)/\kappa^2]$, where Ryo is Rydberg for hydrogen. Hence, the Wigner gap width is estimated to be $\Delta_{Wigner\text{-}gap}=6.1$ meV. This value is nearly equal to the energy gap $\Delta_{Wigner\text{-}gap}=5.8$ meV obtained from the noise measurement. The temperature dependence of electrical conductivity for boron-doped diamond has been measured (see Ref. 10) and is shown in Fig. 4. From the figure the conduction process in the WC can be observed below about 30 K (see "unirrrad." in Fig. 4). It is generally assumed that the Wigner lattice is nonconducting at $T=0$ K in the presence of a gap against single particle excitations. However, our results indicate that the transition from liquid to crystalline state is not accompanied by a sudden reduction of conductivity to zero. An estimate of the activation energy has been made using the straight line A in Fig. 4. The magnitude of the activation energy is 5.5 meV and this value is in good agreement with $\Delta_{Wigner\text{-}gap}=5.8$ meV obtained from the noise measurement. Furthermore, the temperature dependence of electrical conductivity for boron-doped diamond of phosphorus implantation dose 3.80×10^{14} ions/cm^2 is shown by "irrad." in Fig. 4. The specimen was irradiated with 150 MeV P^{+9} ions using the Tandem accelerator at JAERI-Tokai. The temperature of the specimen during ion irradiation was kept at 20 K. In the case of irradiated specimen a noticeable change was not observed around 30 K. Moreover, the single activated conduction in the presence of the hard gap of width 10.7 meV appears in the lowest temperature region of the measurement as shown by the straight line B in Fig. 4. The data show a trend from collective to single-particle state with increasing disorder from A to B in Fig. 4.

If thermal energy k_BT exceeds the value of the Wigner gap width, the long-range order of the Wigner lattice breaks down and the resulting fluid phase (i.e., random configuration of carriers) appears. We can get a qualitative picture of the shape and nature of the phase diagram in terms of ratio of potential energy V to the kinetic energies K in the liquid phase, i.e., $V/K=\Gamma_0$. For the present case, a 3D hole liquid with a density per unit volume n in the presence of a uniform negative background, the potential is approximated by $V=(e^2/\kappa)(4\pi n/3)^{1/3}$. On the other hand, the mean kinetic energy per particle is $K=k_BT$ in high temperature classical regime. The fluid-solid phase transition is simply described in terms of $\Gamma_0=(e^2/\kappa)(4\pi/3)^{1/3}n^{1/3}/k_BT$. Hence, the melting line in the $n-T$ plane, that is the fluid-solid coexistence line, is given by $n=(3e^{-6}\kappa/4\pi)(\Gamma_0k_BT)^3$. The current fluctuations are proportional to fluctuations of the carrier number $\delta n(t)$. The spectral density of the current fluctuations at frequency f, S_I, is related to the correlation function of $\delta n(t)$ at frequency f by $S_I(f)/I^2\propto\langle\delta n(t)\delta n(t')\rangle_f$, where $\langle\ \rangle_f$ denotes the Fourier transform of the correlation function, and I is the mean current. If we assume the fluctuations of carrier δn to be proportional to the number of melted carriers, then $S^{1/2}$ should be proportional to T^3. Actually, we have observed $S^{1/2}$ to be nearly proportional to T^3 below 67 K, so we can expect that the liquid is coexistent to WC below 67 K.

In Fig. 5 we show the temperature dependence of eigenfrequency modes of the voltage noise power density. In this temperature range there appear three eigenfrequency modes around 25 Hz. These modes start appearing at 70 K, take maximum around 60 K, and disappear at 40 K. In the case of neutral systems, the surface-energy density is positive. Therefore, in equilibrium, the system should have a minimal area of the surface separating the phases, leading to global phase separation. On the other hand, in the 3D charged systems, the global phase separation is impossible because of the large Coulomb energy associated with charge separation. Spivak[41] proposed the existence of an intermediate phase between the Fermi-liquid and the Wigner crystal phases due to this partial separation of uniform phases. Below the transition point, the holes which are close enough to the boundary do not satisfy the Wigner crystallization condition and should be in the liquid state. This means that the sharp edge

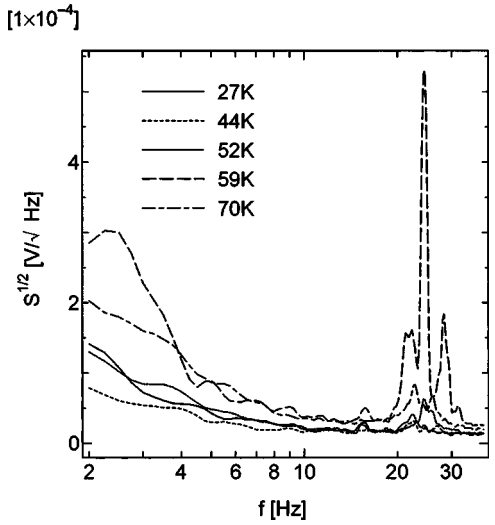

FIG. 5. Temperature dependence of eigenfrequency modes.

of a Wigner crystal should be surrounded by a thin film of hole liquid. In this case, two kinds of motion are possible. One type of motion is fluid oscillations within the surrounding film. Another type of motion involves the displacements of the WC solid. We first consider the fluid motions. Ortiz *et al.*[42] analyzed the stability of different phases of 3D nonrelativistic electron gas by using stochastic methods. There is a continuous transition from the ferromagnetic fluid to the ferromagnetic WC at $r_s=65$. Similarly, Ceperley *et al.*[22] have reported that the fermion system shows phase transition from liquid to crystal solid at $r_s=100$, and the polarized ferromagnetic Fermi fluid is stable between $r_s=75$ and $r_s=100$. According to their results, the fluid within the surrounding film must be polarized ferromagnetic. If the polarized ferromagnetic Fermi liquid appears around the boundary, there may exist the correlated motion of holes. This may be the cause of the generation of the eigenfrequency modes.

Next, we consider the motion due to displacement of the WC solid. Tsuruta *et al.*[43] showed that Coulomb clusters could have particularly stable microstructures with good spherical symmetry at certain number of particles. However, they did not investigate the thermal and dynamic stability of the configuration of particles. Because 2D clusters of particles can exhibit a number of normal modes, we consider here 2D clusters. For a system consisting of a finite number of repelling particles restricted to 2D, the cluster patterns are determined by the need to balance the tendency to form a triangular lattice against the formation of a compact circular shape. The configuration is determined by these two competing effects, namely, circular symmetry and triangular structure (Wigner lattice). This competition leads to intrinsic defects in 2D circular Coulomb clusters which are geometry induced defects. Kong *et al.*[44] investigated the effects of geometry induced defects on eigenfrequency modes for large clusters. In this system, there are three eigenfrequency modes which correspond to the rotation of the system as a whole, the center of mass mode, and the breathing mode, respectively. As shown in Fig. 5, we can observe that there are three large eigenfrequency modes at around 25 Hz at 59 K. These eigenfrequency modes certainly indicate the existence of the correlated motion of carriers below 67 K. Now, we cannot determine whether these modes are caused by polarized ferromagnetic Fermi liquid surrounding the Wigner cluster or normal modes within the Wigner cluster. If ferromagnetic Fermi liquid is the source of eigenfrequency modes, the magnetic susceptibility should rapidly change from negative to positive around 60 K, because susceptibility demonstrates diamagnetism in the hopping region.

The mean potential energy which is the mean interaction energy between two holes in our diamond is approximated by $V=107$ meV. As shown in Fig. 5, eigenfrequency modes disappear at 40 K. It is understood that WC grows, extending to the entire crystal in our sample at this temperature. Therefore, complete formation of the Wigner crystal is expected to occur around 40 K. In the high-temperature classical regime where the kinetic energy is given by $K=k_BT=40k_B$, the constant Γ_0 is equal to $\Gamma_0=V/k_BT=175$ for the $\kappa=1$ system. In classical 3D gas, Brush *et al.*[45] studied the equilibrium states of a one-component plasma of ions moving in a uniform neutralizing background using the Monte Carlo method and obtained $\Gamma_0=125$ for the occurrence of fluid-solid phase transition. Pollack *et al.*[46] obtained $\Gamma_0=155$. Furthermore, the predicted value of Γ_0 from the results of Monte Carlo computer simulations is $\Gamma_0=178-180$.[47,48] Hence our value agrees with the theoretical values. The crystallization of carriers takes place basically through competition between long-range Coulomb interactions and kinetic energy. Once the system is in lattice configuration, the main part of the binding energy as well as of the force governing the carrier motion arise from the interaction of the carrier with the background in its immediate vicinity. De Wetts[49] has shown that the spherical approximation, in which each carrier is considered to reside in a spherical cell and in which all interactions between cells are neglected, accounts for 99.5% of the electrostatic binding energy. Thus, a solid arrangement may be characterized by the picture that each charge is constructed from a sphere with radius of effective Wigner–Seitz distance r_s as if the carrier has a hard repulsive core.

In summary, this paper describes noise properties of a boron-doped diamond as a function of temperature. From the experimental results, the following conclusions are obtained:

(1) We have proved the existence of the hard gap.

(2) We have shown the possibility of Wigner lattice transition.

Our experimental evidence for the existence of hole crystallization gives an answer to the question raised more than 70 years ago.[20] That is, a 3D Wigner lattice certainly exists in real solid materials at zero magnetic field.

ACKNOWLEDGMENTS

We are grateful to Professor Michiko Inoue and Mami Kojima for many helpful discussions on the subject of this paper. We also thank the technical staff of the Tandem Accelerator Division at JAERI-Tokai for their great help.

*Present address: Moririca Electronics, Ltd., Izumi-cho 3321, Izumiku, Yokohama 245-8501, Japan.
†Corresponding author.

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