Electron spin resonance in graphite

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Electron spin resonance in three- and quasi-two-dimensional graphites has been investigated between liquid-helium and room temperatures. The g shift (Δg) of three-dimensional graphite first increases with lowering temperature (T) so as to form a peak at 20 K, and then steeply falls off. An expression for $\Delta g(T)$ proposed on the basis of the Dresselhaus-Dresselhaus Hamiltonian implies that the peak is produced in a way similar to that for the diamagnetic susceptibility. Curve fitting to the data, in which the divergence of the E_3 band is removed by considering the energy uncertainty, reproduces the temperature dependence fairly well by using the spin-orbit coupling constants with the correct order magnitude but with negative sign. The origin of such a difficulty involved in the calculation is discussed in connection with subtle balance between the electron and hole contributions. Specimens of quasi-two-dimensional graphite show behavior of Δg-versus-T similar to that observed for the three dimensional; this behavior is affected by localized spins especially at low temperatures. The absorption lines of all the specimens examined are narrowed with increasing temperature above 20 K by an averaging process of the g values of conduction carriers in k space.

I. INTRODUCTION

The conduction-electron spin resonance (CESR) of graphite in the temperature range from 77 up to 600 K was investigated as early as 1960 by Wagoner[1] using a natural single-crystal specimen. After that, a number of authors[2–4] made similar studies on a variety of well-defined specimens of graphite, and have obtained nearly the same results. First, the absorption line is of typical Dyson form and indicates a large g anisotropy. The g value with a magnetic field in the c direction is about 2.05 at room temperature and increases monotonically with lowering temperature so as to exceed 2.10 at 77 K while that with the field perpendicular to the c axis shows almost no shift from the free-electron value 2.0023 independent of temperature. Second, the linewidth when the field is in the c direction is as narrow as 5~6 G near 300 K and increases remarkably with lowering temperature; thus the detection of the signal is made fairly difficult below 77 K.

In order to account for Wagoner's results, McClure and Yafet[5] proposed a theory based on the band model of Sloncewski and Weiss[6] (hereafter referred as SW), taking into consideration the admixture of the $3d$ state with the π orbital. They pointed out that the observed g value is an average of the contributions of electrons and holes, which are both expressed as functions of their wave vectors and have opposite signs to each other. However, we have found out that McClure-Yafet's formulation leads to some difficulties, for instance, that divergence of the g shift takes place at the singular point of $E=E_3$. Hence, the validity of the theoretical curve demonstrated in their paper is still of some doubt, and the problem seems not to have been resolved yet.

In the following sections we present the results of our CESR measurement recently performed over the temperature range from 300 K down to far below 77 K using four kinds of well-oriented graphite specimens. A theoretical analysis of the data is made on the basis of a formalism for the g shift, in which the difficulty of divergence is removed by taking into account the uncertainty of energy. Qualitative discussion is also given of the ESR characteristics other than the g shift.

II. SPECIMENS AND METHODS

Specimens examined were an iron-melt single-crystal graphite (the so-called Kish graphite, hereafter KG), highly oriented pyrolytic graphite (HOPG), and pyrolytic graphites as-deposited at 2100 and 2300 °C (PG2100 and PG2300), respectively. As-deposited PG's are much less crystalline than KG and HOPG, but the basal planes are aligned nearly in parallel so as to form a quasi-two- dimensional structure. Test pieces were cut in the form of thin rectangular plates of dimensions of $2\times5\times0.1$ mm^3.

The ESR measurement was performed with a JES-FE1XG spectrometer operated in the TE_{001} mode at temperatures below 300 K using liquid helium as coolant. The intensity of the resonance magnetic field was measured by using an EFM-2000 NMR gaussmeter and the frequency by a TR5212 microwave frequency counter. Absorption lines were analyzed in accordance with the procedure developed by Feher and Kip[7] for the Dyson signal.

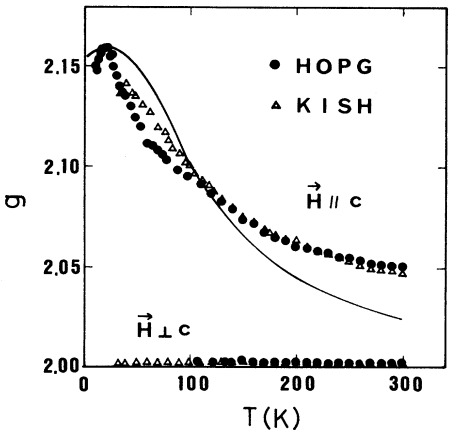

FIG. 1. Temperature dependence of g factors of HOPG and Kish graphite in the presence of magnetic fields parallel and perpendicular to the c axis, respectively. Results of the curve fitting based on Eq. (11) are represented by a solid line, where the spin-orbit coupling constants obtained are $\lambda_{12}=-4.29\times10^{-4}$ eV and $\lambda_{13}=-5.01\times10^{-4}$ eV.

III. EXPERIMENTAL RESULTS

Figure 1 shows temperature dependence of the g factor of HOPG and KG with circular and triangular marks, respectively. The upper plots represent the data in the presence of a static magnetic field parallel to the c axis, while the lower plots represent those with the perpendicular field. The latter is about 2.003, almost independent of temperature. With the field in the c direction, the g value increases first with decreasing temperature (T) in agreement with Wagoners data above 77 K, but it forms a distinct peak at about 20 K and then falls off leftward.

Figure 2 shows the linewidth (ΔH) versus T for HOPG and KG with the magnetic field applied in parallel to the c axis; the rise of ΔH with decreasing temperature is followed also by a distinct peak at $\sim$20 K in a manner similar to that of the g shift.

In Fig. 3 are demonstrated the g-vs-T plots for as-deposited PG specimens, where the magnetic field is applied along the axis normal to the deposition plane. It should be noted that g values of PG2100 coincide well with those of HOPG all over the temperature range examined. On the other hand, the g values of PG2300 are somewhat less in magnitude, and the peak position is slightly shifted toward the lower temperature side.

ΔH of PG specimens shown in Fig. 4 indicates monotonous leftward rise-up with decreasing temperature but produces no peak in contrast to the plots for HOPG.

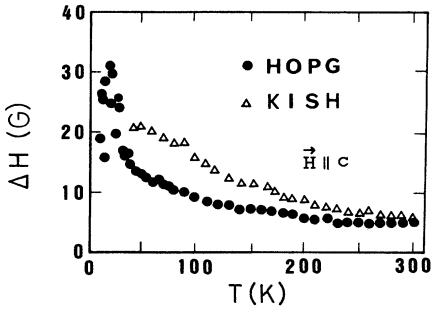

FIG. 2. Linewidth (ΔH) versus temperature plots for HOPG and Kish graphite with the magnetic field azimuth in the c direction.

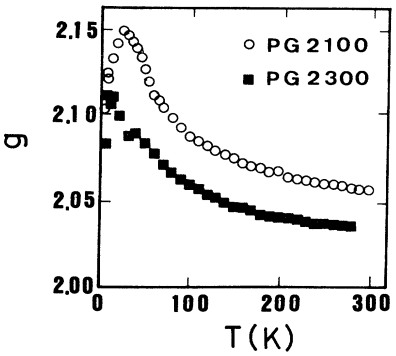

FIG. 3. Temperature dependence of g factors of as-deposited pyrolytic graphites under a magnetic field applied in the direction perpendicular to the deposited surface, PG2100 and PG2300 denote those deposited at 2100 and 2300 °C, respectively.

IV. THEORY AND ANALYSIS

As mentioned in the first section a theory on the g shift (Δg) in CESR of three-dimensional (3D) graphite has been proposed by McClure and Yafet[5] using the SW band model and introducing an admixture of the $3d$ state. Al-

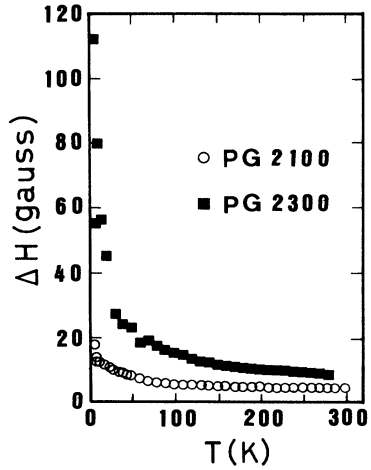

FIG. 4. Linewidth versus temperature plots corresponding to the g versus temperature in Fig. 3 for as-deposited pyrolytic graphites.

though they explained Wagoner's data on this basis we would like to point out two problems overlooked in their work: First, their expression for Δg given as a function of energy (E) of π electrons diverges at $E=E_3$. Second, one has to choose the spin-orbit coupling constant Λ of negative sign to get Δg of positive sign. In the vicinity of $E\simeq E_3$, the contribution of electrons to Δg changes very steeply toward minus infinity, while that of holes changes toward plus infinity.

In the present study expressions for Δg using two spin-orbit coupling constants, λ_{12}^z and λ_{33}^z, on the basis of the Dresselhaus-Dresselhaus Hamiltonian[8] can be calculated as follows. The Dresselhaus-Dresselhaus Hamiltonian takes the form

$$\underline{\mathcal{H}}=\begin{vmatrix} E_1 & \lambda_{12}^z\sigma_z & ip_1\kappa_+ & -ip_1\kappa_- \\ \lambda_{12}^z\sigma_z & E_2 & -ip_2\kappa_+ & -ip_2\kappa_- \\ -ip_1\kappa_- & ip_2\kappa_- & E_3+\lambda_{33}^z\sigma z & 0 \\ ip_1\kappa_+ & ip_2\kappa_+ & 0 & E_3-\lambda_{33}^z\sigma_z \end{vmatrix} , \quad (1)$$

where $p_{1,2}=(\sqrt{3}/2)a_0\gamma_0(1\mp\nu)$, $\nu=(2\gamma_4/\gamma_0)\cos\varphi$, $\varphi=k_zc_0/2$, and σ_z is the Pauli spin matrix. Also,

$$\kappa_\pm=(\kappa_x\pm\kappa_y)/\sqrt{2} , \quad (2)$$

and E_1, E_2, and E_3 (doubly degenerate) are the four bands corresponding to $\mathbf{k}=(0,0,k_z)$; their concrete expressions are given by[6,8]

$$\begin{aligned} E_1&=\Delta+2\gamma_1\cos\varphi+2\gamma_5\cos^2\varphi , \\ E_2&=\Delta-2\gamma_1\cos\varphi+2\gamma_5\cos^2\varphi , \\ E_3&=2\gamma_2\cos^2\varphi . \end{aligned} \quad (3)$$

In the presence of a magnetic field applied parallel to the c axis, the wave-vector components κ_x,κ_y satisfy the commutation relation

$$[\kappa_x,\kappa_y]=\frac{s}{i}, \quad s=\frac{eH}{\hbar c} , \quad (4)$$

and κ_+ and κ_- become the raising and lowering operators:

$$\begin{aligned} \kappa_+u_N&=[(N+1)s]^{1/2}u_{N+1} , \\ \kappa_-u_N&=(Ns)^{1/2}u_{N-1} , \end{aligned} \quad (5)$$

where u_N denotes the harmonic-oscillator wave function.

The eigenvalues in a magnetic field are obtained by solving the following equation:

$$(\underline{\mathcal{H}}-E\underline{I})\begin{bmatrix} u_N \\ u_N \\ u_{N-1} \\ u_{N+1} \end{bmatrix}=0 . \quad (6)$$

Equation (6) leads to the four bands and the g shift is defined by

$$\varepsilon_i'=-\tfrac{1}{2}\Delta g_i\mu_BH\sigma_z , \quad (7)$$

where $E_i=\varepsilon_i^0+\varepsilon_i'$; ε_i^0 is the eigenvalues for $\lambda_{12}^z=\lambda_{33}^z=0$ and ε_i' is the correction term proportional to λ_{12}^z and λ_{33}^z.

The g shifts we are interested in are those associated with E_{2+} (electron band) and E_{1-} (hole band).[9] Imposing the Bohr-Sommerfeld condition

$$\oint d\kappa_x\kappa_y=2\pi s(N+\gamma) \quad (\gamma<1) \quad (8)$$

to the solutions of Eq. (6) we can get the g shifts in the weak-field limit.

For electrons

$$\Delta g_e(E,k_z)=\frac{4m}{\hbar^2}\frac{2\lambda_{12}^zp_1p_2e_3-\lambda_{33}^z(e_2p_1^2+e_1p_2^2)}{e_3(e_2+e_3)[e_1-e_2(p_1^2/p_2^2)]} , \quad (9)$$

and for holes

$$\Delta g_h(E,k_z)=\frac{4m}{\hbar^2}\frac{2\lambda_{12}^zp_1p_2e_3-\lambda_{33}^z(e_2p_1^2+e_1p_2^2)}{e_3(e_1+e_3)[e_2-e_1(p_2^2/p_1^2)]} , \quad (10)$$

where $e_i=E_i-E$. Both formulas are reduced to that of McClure-Yafet by putting $\Lambda\equiv\lambda_{12}^z=\lambda_{33}$.

By use of Eqs. (9) and (10), the total g shift averaged over the Fermi surface is represented as a function of temperature:

$$\begin{aligned} \Delta g(T)&=\sum_{k_z}\sum_E\Delta g(E,k_z)\frac{\partial f_0(E)}{\partial E}\Big/\sum_{k_z}\sum_E\frac{\partial f_0(E)}{\partial E} \\ &=\frac{4m}{\hbar^2}\left[\int_0^{\pi/2}d\varphi\int_{E_3}^{\infty}dE\frac{2\lambda_{12}^zp_1p_2e_3-\lambda_{33}^z(e_1p_2^2+e_2p_1^2)}{2e_3[e_2(p_1^2/p_2^2)-e_1]}\frac{\partial f_0(E)}{\partial E}[p_0^2(1-\nu)^2]^{-1}\right. \\ &\quad\left.+\int_0^{\pi/2}d\varphi\int_{-\infty}^{E_3}dE\frac{2\lambda_{12}^zp_1p_2e_3-\lambda_{33}^z(e_1p_2^2+e_2p_1^2)}{2e_3[e_2-e_1(p_2^2/p_1^2)]}\frac{\partial f_0(E)}{\partial E}[p_0^2(1+\nu)^2]^{-1}\right] \\ &\quad\Big/\left[\int_0^{\pi/2}d\varphi\int_{E_3}^{\infty}dE[E-(E_2+E_3)/2]\frac{\partial f_0(E)}{\partial E}[p_0^2(1-\nu)^2]^{-1}\right. \\ &\quad\left.+\int_0^{\pi/2}d\varphi\int_{-\infty}^{E_3}dE[(E_1+E_3)/2-E]\frac{\partial f_0(E)}{\partial E}[p_0^2(1+\nu)^2]^{-1}\right] , \end{aligned} \quad (11)$$

where f_0 is the Fermi-Dirac function and

$$p_0=\frac{\sqrt{3}}{2}a_0\gamma_0 .$$

The band-parameter values used in the following calculation are as given in Table I.[9]

In order to remove the aforesaid difficulty of divergence we put

$$E_3-E=\pm\sqrt{(E_3-E)^2+\Gamma^2} , \tag{12}$$

where $\Gamma\sim\hbar/\tau$ represents the uncertainty of energy, and we assume that τ is the same order as the relaxation time of carrier scattering.

The dashed line in Fig. 1 shows the results of curve fitting to the temperature-dependence data for the g value of the HOPG using Eq. (11), where λ_{12}^z, λ_{33}^z, and Γ have been determined through the least-squares method. The reproducibility is fairly good, and the coupling constants λ_{12}^z and λ_{33}^z obtained are -4.29×10^{-4} eV and -5.01×10^{-4} eV, respectively. These values are of correct order in the magnitude, but the sign is still negative, the same as in McClure-Yafet's theory. A theoretical explanation of this sign problem will be given later in the next section. Also the uncertainty of energy is computed at 2.56×10^{-4} eV. This value corresponds to $\tau=2.5\times10^{-12}$ sec which is a reasonable order-of-magnitude estimate for the conductivity relaxation time in graphite.

In Fig. 2 we have found that the plot for PG2100 is almost the same as that for 3D graphite. Such a result is not readily anticipated from its crystal structure. As is generally known, as-deposited PG is of quasi-two-dimensional structure unlike HOPG, and contains more lattice defects; these defects are probably associated with localized spins whose contribution to ESR may become not negligible at low temperatures. Hence, the apparent agreement seems to be fortuitous, and has to be considered on a basis other than that for 3D graphite.

Denoting the g value of localized spin centers by $g_{\rm loc}(=2.0023)$ and that of conduction carriers by $g_{\rm cond}$, Mrozowski[10] has proposed that observed g value can be expressed as a sum of their fractional contributions in the following form:

$$g_{\rm obs}=g_{\rm cond}\frac{\chi_{\rm cond}}{\chi_{\rm loc}+\chi_{\rm cond}}+g_{\rm loc}\frac{\chi_{\rm loc}}{\chi_{\rm loc}+\chi_{\rm cond}} . \tag{13}$$

In this formula, $\chi_{\rm loc}$ is the paramagnetic susceptibility due to localized spins and obeys the Curie law

$$\chi_{\rm loc}(T)=\frac{A}{T} , \quad A=\frac{N_{\rm loc}g^2\mu_B^2S(S+1)}{3k_B} , \tag{14}$$

where $N_{\rm loc}$ is the number of localized spin centers, μ_B the Bohr magneton, and k_B the Boltzmann constant and S is taken to be $\frac{1}{2}$. On the other hand, $\chi_{\rm cond}$ is for the Pauli paramagnetism and written as

$$\chi_{\rm cond}(T)=\frac{\mu_B}{2H}[N(\downarrow)-N(\uparrow)]$$
$$=\frac{\mu_B}{2H}\int_0^\infty dE\,D(E)[f_0(E+\mu_BH)-f_0(E-\mu_BH)] , \tag{15}$$

where $N(\uparrow)$ and $N(\downarrow)$ represent the number of up and down spins, respectively, and $D(E)$ is the density of state.

Making use of Wallace's linear band model[11] for 2D graphite with the dispersion relation

$$E=p_0k , \quad E_h(E)=\frac{E}{c_0\pi p_0^2} , \tag{16}$$

where c_0 is the interlayer distance, one can rewrite Eq. (15) as

$$\chi_{\rm cond}(T)=-\frac{\mu_B^2}{\pi c_0p_0^2}\int_0^\infty E\frac{\partial f}{\partial E}dE\approx\frac{\mu_B^2N}{E_F} \tag{17}$$

in an approximation valid at low temperatures. Here E_F denotes the Fermi level and $N=N(\uparrow)+N(\downarrow)$ is the carrier density, which can be evaluated from the data of the zero-field Hall coefficient. Through analyses of the characteristic diamagnetism and negative magnetoresistance,[12] E_F of PG2100 has been computed at -5 meV from the valence-band edge, and it enables estimation of $\chi_{\rm cond}(T)$.

As pointed out by Kazumata,[13] the absorption-intensity ratio between temperatures T and T' is expressed as

$$R=\frac{I(T)}{I(T')}=\frac{\chi_{\rm cond}(T)+\chi_{\rm loc}(T)}{\chi_{\rm cond}(T')+\chi_{\rm loc}(T')} , \tag{18}$$

which can be determined through a comparison of the areas of absorption peaks on the chart. In Fig. 5 we show the relative intensity of PG2100 as a function of T below 50 K. Circles represent the experimental data, which are noted to indicate a minimum at about 35 K.

From Eqs. (14), (17), and (18) in combination with the relative-intensity data, we have calculated $\chi_{\rm cond}(T)$ and $\chi_{\rm loc}(T)$ as shown by dashed and broken lines in Fig. 5, respectively, where parameter A was determined by using the observed intensity ratio between 4.2 and 35 K (minimum point); the calculated total susceptibility in the range below 50 K is shown by a solid line.

Thus, the contributions of the two kinds of spins to the g value of PG2100 are separated on the basis of Eq. (13).

TABLE I. Slonczewski-Weiss band parameters used in calculation of $\Delta g(T)$ of 3D graphite (Ref. 9).

γ_0	γ_1	γ_2	γ_4	γ_5	Δ	E_F
3.16	0.39	−0.02	0.044	0.038	−0.008	−0.024

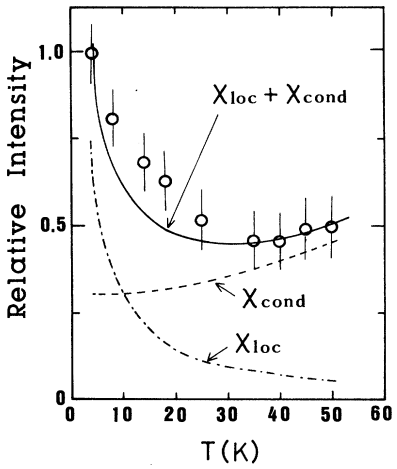

FIG. 5. Relative intensity of the absorption line of PG2100 at temperatures below 50 K. Circular marks represent the experimental data, while lines are for results of the theoretical analysis as indicated.

Numerical values of $g_{\rm cond}(T)$ thereby calculated are given in Table II; its magnitude increases monotonically with decreasing temperature in the range down to 4.2 K. Such behavior is quite different from that of HOPG for which $g_{\rm obs}(T)=g_{\rm cond}(T)$ exhibits a peak at 20 K as an intrinsic nature of the carrier system. Namely, the fall-off of the g value of as-deposited PG's to the left of the peak value in Fig. 2 is due to the contribution of localized spins which become dominant at low temperatures in accordance with the Curie law.

V. DISCUSSION

In McClure-Yafet's theory,[5] the g shifts caused by electrons and holes with a magnetic field in the c direction are opposite to each other, and become zero in total for 2D graphite if the graphite is completely compensated. McClure[14] corrected this conclusion later by taking into account the contribution of the spin-orbit splitting of the Landau level at the band degeneracy ($n=0$), and has derived an expression for the total g shift of 2D graphite as follows:

$$\Delta g=\frac{\alpha\Lambda}{k_BT}\left[\frac{-\dfrac{p_0^2m}{\hbar^2k_BT\cosh^2\dfrac{x_0}{2}}+\alpha\tanh\dfrac{x_0}{2}}{2\ln\left(2\cosh\dfrac{x_0}{2}\right)}\right], \quad (19)$$

where $x_0=E_F/k_BT$, m is the electron mass, α is the admixture coefficient of $3d$ functions in the π band, and others are as customarily used. (There were some mistakes in McClure's original expression that have been corrected in the above.) The first term in the numerator in large parentheses represents the contribution from the $n=0$ Landau level; this predominates over the second term, which corresponds to those from other levels. One can readily see that such a situation is quite similar to that of the characteristic diamagnetism of graphite, in which the formation of the $n=0$ Landau level due to the band-to-band transition plays an important role. In fact, McClure also gives an expression of the g shift in relation to the anisotropy of the diamagnetic susceptibility.

In the case of 3D graphite, it is not possible to separate the two terms so distinctly in Eq. (11), but the underlying mechanism seems essentially the same: As in the case of diamagnetism, the carrier population of the $n=0$ Landau level is increased by thermal excitation from the Fermi level, and gives rise first to an increase of $\Delta g(T)$ with raising temperature in the range up to the peak position near 20 K. Further elevation of temperature beyond it tends to distribute these carriers over the higher-number levels so as to reduce the dominant contribution of the $n=0$ level, leading to the right-hand fall-off of the g versus T plot as observed in Fig. 1.

In this context we may consider the foregoing problem that the sign of spin-orbit coupling constants λ_{12}^z and λ_{33}^z in Eq. (11) apparently had to be chosen negative in the procedure of curve fitting to the experimental data of $\Delta g(T)$. Equations (9)–(11) for the g shift were obtained from the eigenvalues $E_n(k_z)$ of the SW band model in the presence of a magnetic field imposing the semiclassical condition given by Eq. (8). Such a procedure based on

TABLE II. Numerical values of $g_{\rm loc}$ of PG-2100 between 4.2 and 50 K estimated by using Eq. (13) in combination with experimental and analytical results shown in Fig. 3 and 5, respectively.

T (K)	$\chi_{\rm cond}(\times10^{-8}$ emu/g)	$\chi_{\rm loc}(\times10^{-8}$ emu/g)	$g_{\rm cond}$
4.2	0.918	2.104	2.3367
8.0	0.924	1.105	2.2720
14.0	0.935	0.631	2.2222
18.0	0.963	0.491	2.2135
25.0	1.032	0.354	2.1721
35.0	1.144	0.253	2.1746
40.0	1.219	0.221	2.1647
45.0	1.294	0.196	2.1540
50.0	1.384	0.176	2.1436

the orbital quantization hypothesis is valid for the Landau levels with $n \gg 1$, but not accurate enough for those levels with $n \sim 0, 1$, which correspond to $E \sim E_3(k_z)$. The latter may play a rather essential role in the estimation of the electron and hole contributions which virtually cancel each other in Eq. (11) for the total g shift. It is noted that we cannot get a field-independent Δg for 3D graphite from the procedure.

$$\Delta g = \lim_{n \to \infty} \sum_{\substack{n=0 \\ n \neq 0}} \sum_{k_z} \Delta g(n, k_z) \frac{\partial f_0[E(n,k_z)]}{\partial E} \Big/ \sum_{n} \sum_{k_z} \frac{\partial f_0[E(n,k_z)]}{\partial E} . \tag{20}$$

If this is applied to 2D graphite, both contributions of the $n=0$ and $n \neq 0$ levels lead to the field-independent values as shown by Eq. (19); it is not the case in 3D graphite, however.

In consequence, an approximate calculation taking into account not exactly enough the low-number Landau levels ($n \sim 0, 1$) may lead to the negative g shift whose temperature dependence is nearly in agreement with the observed data. In a word, since $\Delta g_e < 0$ and $|\Delta g_e| \sim \Delta g_h \gg |\Delta g| = |\Delta g_e + \Delta g_h|$ in Eq. (11), a slight change of Δg_e and/or Δg_h in the calculation may change the sign of the total Δg. Such a situation is somewhat similar to that of the thermoelectric power (S) of graphite,[15] where $S = S_e + S_h$ and $|S_e| \sim S_h \gg |S_e + S_h|$. In KG and/or HOPG, S exhibits a pronounced negative dip due to the phonon-drag effect around 30–40 K; slight neutron irradiation ($\sim 10^{16}$ nvt) shifts the whole plot upward so as to make $S > 0$ below 300 K, but the temperature-dependence behavior is similar to that before the irradiation.

Thus, although our calculation using such negative values for the spin-orbit coupling constants is conventional, it can still be expected reasonably to provide a qualitatively correct temperature dependence of the g shift.

The g shift in as-deposited PG's shown in Fig. 3 is concluded, through a phenomenological analysis in the last section, to be a sum of contributions of conduction carriers and localized spins. However, g_{cond} phenomenologically determined as in Table II behaves in a manner different from that for 3D graphite such as HOPG, reflecting the structural difference between them. An attempt to reproduce g_{cond} as a function of temperature using Eq. (20) for ideal 2D graphite has failed in yielding any success; the calculation with appropriate parameter values gave rise to a remarkable shift of the g-vs-T diagram and also of its peak position toward a higher temperature side.

In connection with this, Kotosonov[16] has recently measured ESR of his own PG specimens and analyzed the data on the basis of the 2D band model. In order to fit the theory to experiment, he proposed to take into account smearing of the state density due to the defect scattering of carriers, and introduced a concept of the effective temperature $T + \delta$ in dealing with thermal excitation of carriers to the $n=0$ Landau level. In fact, by further considering the minor contribution of some localized spins, he was able to reproduce all the data using Eq. (19), though δ amounted sometimes up to 300 ~ 1000 K. Such a picture for smeared energy levels has something in common with that of Bright[17] who has accounted for the negative magnetoresistance of some pregraphitic carbons. However, the smearing as broad as 300 K seems far beyond that anticipated by Bright, and in the case of our PG2100 and -2300 the Fermi levels obtained from the g shift become much deeper than those evaluated through an analysis of their negative magnetoresistance data.[12] More studies are needed to remove the numerical discrepancy between both analyses. The right-hand descending trend of ΔH-vs-T plots for all the specimens over the most part of the temperature range examined is undoubtedly due to the motional narrowing effect which is more enhanced by the phonon scattering with increasing temperature. However, the reason why ΔH of HOPG exhibits a peak at about 20 K coincidently with that of $\Delta g(T)$ is not clear at present. There might be some connection with the fact that the lineshape parameter A/B of the Dyson-type signal tends to become less than the critical value 2.55 below 20 K, making it hard to determine precisely the linewidth. On the other hand, the reason why the line width of PG2300 is larger than that of PG2100 can be attributed appropriately to the relatively inhomogeneous structure of the former. X-ray-diffraction measurement has turned out that PG2300 gives a composite profile of (002)-reflection line and hence is a mixed-phase structure consisting of 3D and 2D components, while PG2100 is rather uniformly of quasi-2D structure.[18]

VI. CONCLUDING SUMMARY

The conduction electron spin resonance in Kish graphite, HOPG and as-deposited pyrolytic graphites was measured between liquid-helium and room temperatures. The g shift (Δg) in Kish graphite and HOPG, which show 3D stacking order of basal planes, has been observed not only to increase with lowering temperature (T) but to exhibit a distinct peak at 20 K in the presence of magnetic field parallel to the c axis, while that with the perpendicular field was negligible.

A theoretical expression of $\Delta g(T)$ based on the Dresselhaus-Dresselhaus Hamiltonian is proposed to improve McClure-Yafet's formula using two constants of the spin-orbit coupling; where the mechanism underlying the peak formation at 20 K is concluded to be something common with that of the diamagnetic susceptibility. In

the curve fitting to the data, the divergence of Δg at $E=E_3$ is removed by taking into account the energy uncertainty connected with the scattering of carriers in their cyclotron motion. The calculation reproduces the temperature dependence of Δg fairly well, while the spin-orbit coupling constants employed are of the correct order in the magnitude but negative in the sign. The origin of the difficulty leading to such a choice of the sign is discussed in connection with the following facts: $\Delta g(T)$ is given as a subtle balance between the large contributions of electrons and holes, and its expression in the form of Eq. (11) for 3D graphite is obtained through a procedure valid for the Landau levels with relatively high quantum numbers but is not accurate enough for the low-number levels.

As-deposited pyrolytic graphites, whose structure is rather quasi-2D, exhibit g-vs-T plots similar to that of 3D graphite both in the magnitude and the curve shape. However, the peak formation near 20 K is correlated rather to the localized spin centers which are associated with the structural defects and contribute dominantly at low temperatures in accordance with Curie law. The right-hand descent of the linewidth versus temperature plots observed for all the specimens is attributed to the motional narrowing effect through an averaging process of g values of scattered carriers over the Fermi surface.

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[1]G. Wagoner, Phys. Rev. **118**, 647 (1960).
[2]M. Murata, Thesis of Master of Science, Institute of Materials Science, University of Tsukuba (unpublished) (1982).
[3]L. S. Singer and G. Wagoner, J. Chem. Phys. **37**, 1812 (1962).
[4]K. Kawamura, S. Kaneko, and T. Tsuzuku, J. Phys. Soc. Jpn. **52**, 3936 (1983).
[5]J. W. McClure and Y. Yafet, in *Proceedings of the 5th Conference on Carbon,* edited by S. Mrozowsky and P. L. Walker (Pergamon, Oxford, 1962), Vol. 1, p. 22; Y. Yafet, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 14, p. 2.
[6]J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958).
[7]G. Feher and K. Kip, Phys. Rev. **98**, 337 (1954).
[8]G. Dresselhaus and M. S. Dresselhaus, Phys. Rev. **140**, 402 (1965).
[9]G. Dresselhaus and M. S. Dresselhaus, Adv. Phys. **30**, 139 (1981).
[10]S. Mrozowski, Carbon **3**, 305 (1965).
[11]B. T. Kelly, *Physics of Graphite* (Applied Science Publishers, London, 1981), Chap. 5.
[12]K. Matsubara, K. Kawamura, and T. Tsuzuku (unpublished).
[13]Y. Kazumata, J. Phys. Chem. Solids **44**, 1025 (1983).
[14]J. W. McClure (unpublished).
[15]K. Kawamura, H. Oshima, and T. Tsuzuku, J. Phys. Soc. Jpn. **42**, 1669 (1977).
[16]A. S. Kotosonov, Zh. Eksp. Teor. Fiz. **93**, 1870 (1987) [Sov. Phys. JETP **66**, 1068 (1987)]; Carbon **26**, 735 (1988).
[17]A. A. Bright, Phys. Rev. B **20**, 5142 (1979).
[18]M. Shiraishi (private communication).