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Electrical resistance in the c direction of graphite

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The c-axis resistivity (ρ_c) and its temperature dependence of highly oriented pyrolytic graphite have been studied in connection with the characteristic stacking-fault structure. In order to account for the observations, the pioneering theory of Ono on the tunneling conduction through the stacking-fault planes is reformulated using the concept of effective fault spacing. It is proposed further to add two mechanisms to the Ono theory; one is interlayer charge transfer through the impurity-assisted hopping of carriers similar to that previously considered for graphite intercalation compounds, and the other is thermal excitation of carriers across the low potential barrier formed on each fault plane. All the data have been satisfactorily reproduced by the curve fitting based on the formula consisting of these three conduction components. Also, the change of ρ_c in the presence of high pressure is pointed out to be qualitatively explainable in terms of the tunneling associated with the pressure dependence of Slonczewski-Weiss band parameters.

I. INTRODUCTION

Although a number of studies have been made so far on the c-axis resistivity (ρ_c) of graphite, the data are scattered over a wide range from 10^{-3} to 10^{0} Ω cm, making a sharp contrast with those on the in-plane resistivity (ρ_a), which indicate coincidently $\rho_a \sim 5\times10^{-5}$ Ω cm at room temperature. According to Primak and Fuchs[1] and Tsang and Dresselhaus,[2] the order of ρ_c of natural and/or synthetic single crystals of graphite is $10^{-3}\Omega$ cm and shows a metalliclike dependence on temperature (T). On the other hand, specimens of highly oriented pyrolytic graphite (HOPG) show $10-10^2$ times higher values of ρ_c than those of single crystals, and exhibit a strange behavior that ρ_c increases first with T up to 50 K, and then decreases in the following temperature range above it.[3,4]

Straightforward application of the band theory of Slonczewski and Weiss[5] (SW) leads to a conclusion that $\rho_c \simeq 10^2\ \rho_a$ as a result of the anisotropic effective mass of carriers in the k space. This is nearly in agreement with the data on single crystals mentioned above, but is unable to account for the widely scattered ρ_c values of HOPG specimens. Ono[6] has introduced a new concept that the reflection of electron waves by the stacking faults plays an essential role in the c-axis conduction. This mechanism can explain the reason for the widely scattered values of ρ_c from sample to sample within the framework of the SW theory. However, the temperature dependence of ρ_c obtained in his calculation was metalliclike, and hence still discrepant with the observation for HOPG's described above.

Recently, we have reexamined similar calculations on the basis of Ono's theory but in a slightly different form, and found out that ρ_c of the specimen faulted in the stacking order is expected rather to slowly decrease with increasing ambient temperature (T), in contrast to the metalliclike dependence predicted by Ono.[6] This is qualitatively consistent with the apparently semiconductorlike behavior of ρ_c of HOPG's observed at $T<50$ K, but the agreement still leaves much to be desired from a quantitative point of view.

In order to settle those long-pending problems, we have measured ρ_c of several new specimens stepwise different in the perfection, and intended to theoretically reproduce the whole data by adding two mechanisms to Ono's theory. The first is a classical hopping term due to thermal excitation of charge carriers across the low potential barrier formed by the stacking fault, and the second is the so-called impurity-assisted interlayer hopping through the interaction of the carrier system with the in-plane point defects and/or impurity sites. Section II describes the experiments. In Sec. III, the results of our recalculation based on Ono's theory are compared with the data, and consequently the theory modified in combination with the additional two mechanisms is shown to satisfactorily reproduce all the observations. Finally, Sec. IV is the concluding summary.

II. EXPERIMENT

All the specimens examined were HOPG sliced as thin as 0.2 mm or less to avoid troubles stemming from laminar cracks in the resistivity measurement. The in-plane resistivity (ρ_a) was measured by the four-probe method as a function of temperature to evaluate the structural perfection. The data are shown in Fig. 1. The residual resistance ratios (r_R) between room and liquid-helium temperatures were evaluated to be 8.4, 9.4, and 60, respectively; the last one as high as 60 originates from such a low resistivity as $\rho_a = 0.87$ $\mu\Omega$ cm at 4.2 K and seems the best value so far reported, whereas 8.4 and 9.4 are within the range most often observed for HOPG's in past studies.

Figure 2 shows the temperature dependence of the c-axis resistivities (ρ_c) of these HOPG specimens together with those of single-crystal graphite obtained by Primak

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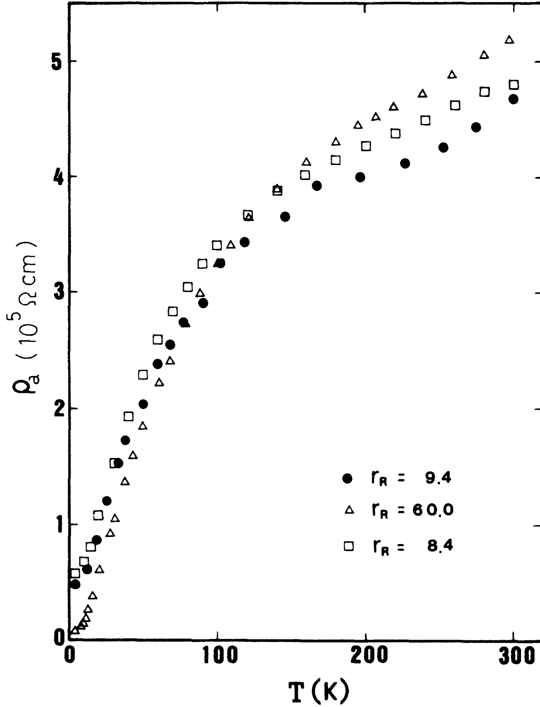

FIG. 1. The in-plane resistivity vs temperature plots for HOPG specimens different in the residual resistance ratio (r_R).

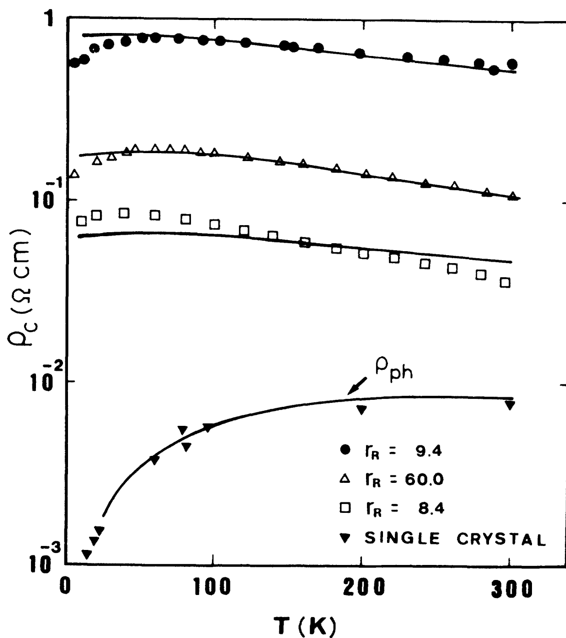

FIG. 2. Semilogarithmic plots of the c-axis resistivity vs temperature for HOPG and single-crystal specimens. Solid lines are results of the curve fitting based on Eq. (2) considering only the carrier scattering by acoustic phonons and stacking faults; discrepancies are still found for unfaulted single crystals, except for the lowest curve (ρ_{ph}).

and Fuchs[1] and Tsang and Dresselhaus.[2] One should note that the specimen with $r_R=60$ shows rather higher values of ρ_c than those of the specimen with $r_R=8.4$ all over the temperature range examined.

III. THEORY AND DISCUSSION

A. Models and formulation

Ono[6] has derived an expression of the c-axis conductivity $1/\rho_c$ as follows:

$$\frac{1}{\rho_c}=\sum_k\left[-e^2\frac{\partial f}{\partial E_k}\right]\tau_{ph}(E_k)v_z^2\left[1+\frac{R}{T}\frac{2\lambda}{l}\right]^{-1}, \tag{1}$$

where τ_{ph} is the relaxation time, v_z the drift velocity, $\lambda=v_z\tau_{ph}(E_k)$ the mean-free-path length of carriers scattered just by acoustic phonons in the c direction, and l the average spacing of stacking faults. R/T represents the reflection versus transmission probability ratio of an electron wave projected onto the stacking fault. Actually, since R exceeds 0.9 for the *ababcac*-type disorder most frequently observed, the incident waves are reflected by the fault plane as if λ were shortened by a factor of more than 10. (Ono[6] has evaluated R and T for three types of stacking fault characteristic of the graphite lattice.)

On the same basis, we define a new parameter $l^*=lT/R$ as the effective fault spacing which equals the carrier mean free path when $\lambda>l$, and rewrite Eq. (1) as follows

$$\frac{1}{\rho_c}=\sum_k\left[-e^2\frac{\partial f}{\partial E_k}\right]v_z^2\left[\frac{1}{\tau_{ph}}+\frac{1}{\tau_{sf}}\right]^{-1}, \tag{2}$$

where $\tau_{sf}=l^*/v_z$. In Ono's original paper, ρ_c calculated as a function of temperature using Eq. (1) is reported to exhibit a metalliclike dependence as illustrated in Fig. 3; the lowest curve for $l=\infty$ seems consistent with the behavior of single crystals, but the upper curves showing high ρ_c values due to the stacking fault are not in agreement with the experimental data for HOPG's. According to Eq. (2), rewritten by the authors, however, ρ_c of such heavily faulted specimens that $\tau_{sf}<\tau_{ph}$ is determined by the temperature-independent parameter τ_{sf}. Since the carrier density of graphite increases through thermal broadening of the Fermi level located in the band-degeneracy region, ρ_c in the $\tau_{sf}<\tau_{ph}$ regime is expected, rather, to decrease with increasing temperature, likewise for a semiconductor, instead of the wholly metalliclike behavior demonstrated in Fig. 3.

Results of the curve fitting procedure based on Eq. (2) are represented by solid lines in Fig. 2, where ρ_{ph} is for the unfaulted specimen with $1/\tau_{sf}=0$ and reproduces almost completely the data for single crystals.[1,2] The upper three curves or HOPG specimens in the present work are fairly close to the observed results above 50 K so as to verify the qualitative expectation stated above. However, one should note a serious discrepancy that the calculation still fails to reproduce the rightward ascending of the experimental plots in the range from 4.2 to about 50 K. Within the framework of Ono's theory, an increase of ρ_c

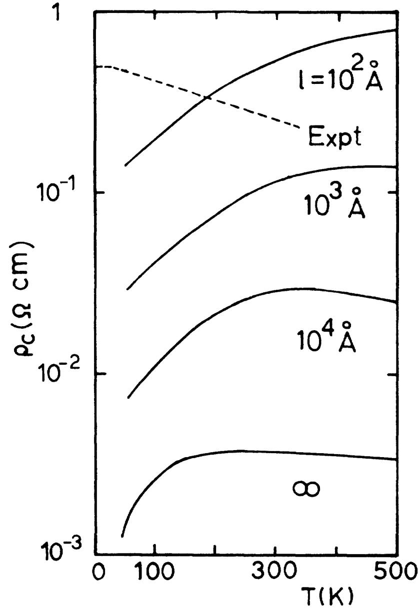

FIG. 3. The c-axis resistivities theoretically calculated by Ono (Ref. 6) for graphite crystals stepwise different in the stacking-fault spacing.

with temperature is ascribed just to the phonon-scattering term $1/\tau_{\mathrm{ph}}$ in Eq. (2), and is represented by ρ_{ph} in Fig. 2 for single crystals. As is readily seen, ρ_{ph} as low as a few $m\Omega$ cm at temperatures below 50 K is less by a factor of 10^1 or 10^2 than the corresponding change of ρ_c of HOPG specimens in the same temperature range. It is therefore necessary to introduce any additional mechanisms of charge transport in the c direction for removal of such a discrepancy.

If the stacking order is faulted every n layers, ρ_c can be represented by the equation

$$\rho_c=[(n-1)\rho_c(\mathrm{GG})+\rho_c(\mathrm{GFG})]/n$$
$$\simeq\rho_c(\mathrm{GG})+[\rho_c(\mathrm{GFG})/n]\ , \tag{3}$$

where $\rho_c(\mathrm{GG})$ denotes the resistivity of unfaulted graphite, and $\rho_c(\mathrm{GFG})$ is that across the fault plane. Now, we assume that the reciprocal of the second term in the right side consists of three components as follows:

$$n/\rho_c(\mathrm{GFG})=n\sigma_c(\mathrm{GFG})$$
$$=n[l^*\sigma_{\mathrm{sf}}/n+\alpha\exp(-\Delta E/k_BT)+\beta\tau_a]$$
$$=l^*\sigma_{\mathrm{sf}}+A\exp(-\Delta E/k_BT)+B\tau_a\ . \tag{4}$$

This equation represents the c-axis conduction across the stacking faults aligned n layers apart. The first term is due to the tunneling current just given by Ono's theory as the T component in Eq. (1). The second term originates in the thermal excitation of carriers over the low potential barrier formed on the plane of stacking disorder;[7] the barrier height ΔE is approximately equal to the SW band parameter $|\Delta|=0.008$ eV representing the potential difference between the two different sites of carbon atoms in the graphite lattice, and the coefficient $A=n\alpha$ is a quantity proportional to the carrier density.

Finally, the third term stands for the interlayer transfer of charge caused by an interaction between the two-dimensionally delocalized carrier system and any defect and/or impurity sites. This is based on a picture similar to the impurity-assisted hopping mechanism[8] or the conduction-path mechanism[9] previously considered for GIC's, and the occurrence of such an interaction depends on how long the lifetime of the stationary state of carriers freely moving in each layer is. In the present calculation, the lifetime is assumed for simplicity to equal the relaxation time of scattering of carriers in the in-plane conduction (τ_a). Since the coefficient $B=n\beta$ is a quantity proportional to the stacking-fault spacing and the carrier density, this term seems to provide a metalliclike component of the temperature dependence.

B. Comparison with experiment

Figure 4 shows results of the curve fitting to the temperature-dependence data for ρ_c of the HOPG specimens using Eq. (4), where numerical values of l^*, A, and B have been determined through the least-square method. One can see that the experimental results are satisfactorily reproduced by the calculation for all the specimens examined: An increase of ρ_c with increasing temperature from 4.2 to 50 K can be ascribed to a decrease of the third term $B\tau_a$ caused by the phonon scattering in the basal plane, while the carrier density remains constant at these low temperatures. Above 50 K, the second term $A\exp(-\Delta E/k_BT)$ becomes dominant so as to lower ρ_c with increasing temperature in combination with a gradual increase of the carrier density.

Table I shows numerical values of the parameters used in the analysis and typical values of each term in Eq. (4) obtained for the three HOPG's: The magnitude of ρ_c of

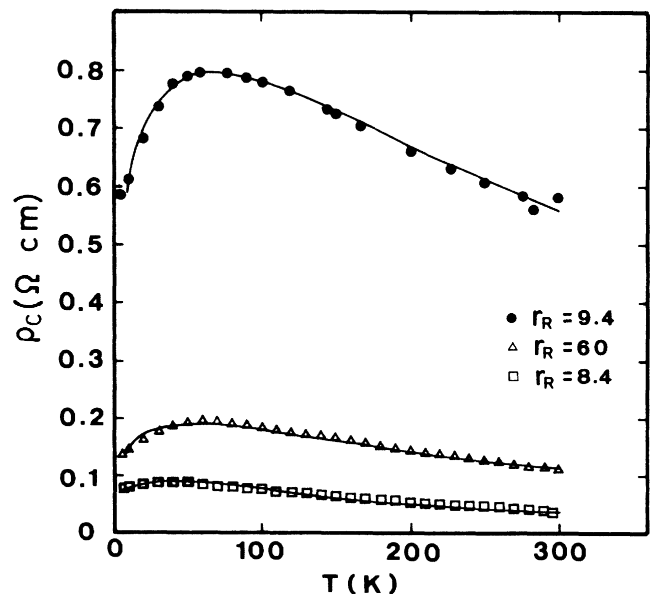

FIG. 4. Curve fitting by the present theory to the c-axis resistivity data for HOPG specimens examined.

TABLE I. Numerical values of the three conduction terms comprising Eq. (4) at various temperatures.

	T(K)	σ_{sf} (Ω^{-1}cm^{-1})	$Ae^{-\Delta E/kT}$ (Ω^{-1}cm^{-1})	$B\tau_a$ (Ω^{-1}cm^{-1})
$r_R=9.4$	10	1.0828	0.0000	5.8474×10^{-1}
$l^*=17.8$(Å)	50	1.1092	0.0000	1.6285×10^{-1}
	100	1.1807	0.0000	1.1131×10^{-1}
	200	1.4229	0.0000	8.5028×10^{-2}
	300	1.7392	0.0000	7.4245×10^{-2}
$r_R=60.0$	10	5.0173	4.8372×10^{-5}	2.1173×10^{0}
$l^*=82.3$(Å)	50	5.1396	9.2675×10^{-2}	1.9226×10^{-1}
	100	5.4710	3.1696×10^{-1}	$1.0834\times^{10^{-1}}$
	200	6.5933	8.7576×10^{-1}	7.2936×10^{-2}
	300	8.0592	1.5311×10^{0}	6.8002×10^{-2}
$r_R=8.4$	10	8.7913	6.0555×10^{-4}	4.8502×10^{0}
$l^*=144.2$(Å)	50	9.0055	1.1602×10^{0}	1.4250×10^{0}
	100	9.5863	3.9679×10^{0}	9.6133×10^{-1}
	200	11.5530	1.0963×10^{1}	7.6636×10^{-1}
	300	14.1211	1.9167×10^{1}	6.7836×10^{-1}

each specimen is mostly determined by the first term as a function of l^* all over the temperature range examined. For instance, $l^*=17.8$ Å for the sample with $r_R=9.4$ corresponds to the actual fault spacing $l=178$ Å if the transmission versus reflection ratio $T/R=0.1$. It should be noted that the temperature-dependent part of σ_{sf} is given just by $\partial f/\partial E_k$ in Eq. (1); consequently, for all the faulted specimens, the higher the ρ_c level, the steeper the gradient of its temperature-dependent plot.

In Table I it is also shown that the thermal excitation component of conduction represented by the second term of Eq. (4) differs very much from sample to sample, and becomes zero for the specimen with $r_R=9.4$; i.e., the negative temperature dependence of ρ_c above 50 K in the last case originates just from an increase of the carrier density included in the first term ($l^*\sigma_{sf}$) for the tunneling across the stacking faults.

As to the hopping conduction component represented by the third term, it is of much interest that the specimen with $r_R=8.4$ shows rather larger values of $B\tau_a$ than those for the highly perfect specimen with $r_R=60$, in spite of its much smaller values of τ_a at low temperatures. This can be interpreted as follows: The low-r_R specimen contains a number of defect and/or impurity sites which make short τ_a at low temperatures. On the other hand, since the interlayer charge transfer takes place as a hopping of carriers through an interaction with such defect sites, one can expect that the lower the r_R, the more the coefficient B proportional to the probability of the interaction, and vice versa. Consequently, the magnitude of the hopping term depends on the delicate balance between the opposite contributions of τ_a and B, but not straightforwardly on the parameter r_R.

Previously, Kawamura *et al.*[3] have examined a number of specimens with different perfection, and found out that the $\ln\rho_c$ versus r_R plot exhibits a Λ-shaped diagram centered at $r_R\sim10$. On this basis, they have proposed an interpretation as follows: In the low perfection specimens with $r_R<10$, the c-axis orientation indicates a little azimuthal spread to that ρ_c is apparently lowered by the tortuous flow of the in-plane current. At $r_R\simeq10$, the parallelism of the basal planes is almost completed, and ρ_c is no longer affected by the in-plane current. Further improvement of the perfection in the range of $r_R>10$ proceeds just as a decrease of the stacking-fault density, and an extrapolation of the plot implies that ρ_c becomes as low as that of unfaulted graphite at $r_R>30$.

However, ρ_c of the present specimen with $r_R=60$ is still high and deviates much from such a Λ-shaped diagram. Therefore, in the case of HOPG's which contain a number of stacking faults on the twist boundary faces, the above explanation given by Kawamura *et al.* is likely valid in the r_R range below ~10, but not beyond it. In other words, r_R can be an indirect measure of the stacking order for the relatively low perfection specimens whose basal planes are slightly tilted with one another, but not for those in which the parallel alignment has been once completed.

C. Pressure dependence

Recently, Uher and Hockey[10] have investigated the temperature dependence of ρ_c of an HOPG between 4.2 and near 300 K under various fixed pressures ranging up to 40 kbar, and obtained the results as in Fig. 5. The overall depression of the ρ_c versus T curve with increasing pressure (p) is qualitatively consistent with the possibility that the tunneling effect across the stacking fault is enhanced by an increase of the overlap of π orbitals resulting from the contraction of the interlayer spacing. On the other hand, the pressure-induced change in its slope leading to a gradual collapse of the peak centered at $T\sim50$ K can be elucidated as in the following paragraphs.

A phenomenological expression of the pressure depen-

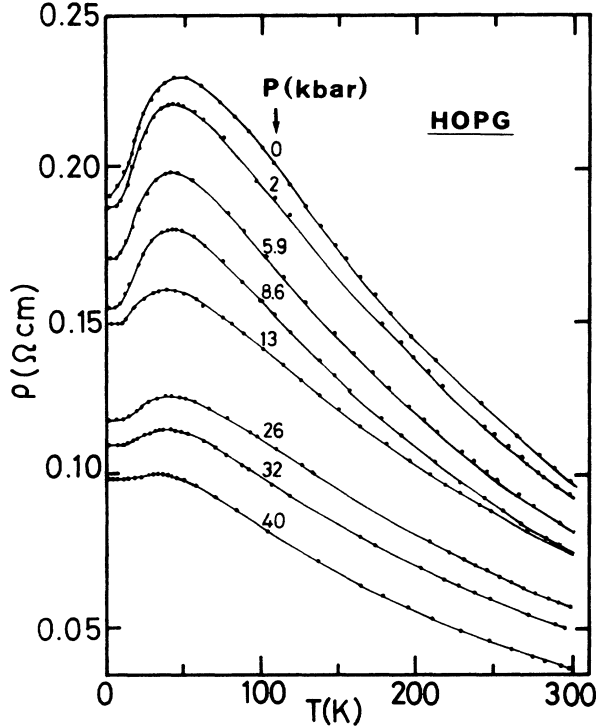

FIG. 5. Temperature dependence of the c-axis resistivity of an HOPG in the presence of high pressure up to 40 kb (Ref. 10).

dence of the conductivity is given by

$$d\ln\sigma/dp \sim d\ln N/dp + d\ln\tau/dp - d\ln m/dp \;, \quad (5)$$

where N denotes the carrier density, τ the relaxation time of scattering, and m the effective mass. Based on the three-parameter band model of Arkhipov, Kechin, and Pospelov[11] using γ_0, γ_1 and γ_2 defined in the SW theory, Noto and Tsuzuku[12] have demonstrated that the next equations hold for the carrier density: At low temperatures where the carrier system is in degeneracy,

$$N \propto \gamma_1|\gamma_2|/\gamma_0^2 \;, \quad (6a)$$

and at high temperatures where $|\gamma_2| < k_B T$,

$$N \propto k_B T \gamma_1/\gamma_0^2 \;. \quad (6b)$$

In the case of the c-axis conduction, m is so large that $d\ln m/dp$ seems as small as the pressure dependence of the compressibility, not more than $\sim 10^{-3}$ kbar, and hence can be neglected in an approximation. Also, since the mean-free-path length is limited by the stacking-fault spacing, one can put $d\ln\tau/dp \sim 0$. Thus, Eq. (5) can be rewritten by using Eqs. (6a) and (6b) as follows; at low temperatures

$$d\ln\sigma/dp \sim d\ln N/dp \sim d\ln\gamma_1/dp + d\ln|\gamma_2|/dp \;, \quad (7a)$$

and at high temperatures

$$d\ln\sigma/dp \sim d\ln N/dp \sim d\ln\gamma_1/dp \;, \quad (7b)$$

where $d\ln\gamma_0/dp$ is neglected in view of the extremely rigid C—C bond in the basal plane. According to the de Haas–van Alphen-effect study by Anderson *et al.*,[13] $d\ln\gamma_1/dp \sim 1.2\times10^{-2}$ kbar and $d\ln|\gamma_2| \sim 2.4\times10^{-2}$ kbar. Therefore, $d\ln\sigma/dp = -d\ln\rho_c/dp$ in the low-temperature regime is about three times larger than that at high temperatures; this is consistent with the fact that the low-temperature peak of the ρ_c versus T diagram in Fig. 5 tends to collapse with increasing pressure.

IV. CONCLUDING SUMMARY

The intrinsic c-axis resistivity of highly perfect crystals of graphite is in the order of 10^{-3} Ω cm with a metalliclike temperature dependence, and the matter can be described in terms of the band theory. In the case of HOPG, however, the resistivities are 10^1-10^2 times higher than the intrinsic value because of the reflection of π-electron waves by the characteristic stacking faults, and their temperature dependence is metalliclike in the range up to about 50 K but semiconductorlike beyond it. In dealing with such high resistivities of HOPG's as a function of temperature, the pioneering theory of Ono[6] on the tunneling of carriers through the fault planes has been reformulated in this study by using the concept of effective fault spacing. This enables to improve somewhat on the theoretical reproducibility for the temperature-dependence data, but still leaves discrepancies which seems unavoidable within the framework of Ono's theory.

In order to remove such a difficulty, two mechanisms of the carrier transport have been newly considered in addition to the tunneling conduction mentioned above. One is the impurity-assisted interlayer hopping conduction, which can be responsible in part, combined with the scattering of carriers by phonons, for the metalliclike temperature dependence of the resistivity below 50 K. The other is due to thermal excitation of carriers across the low potential barrier formed on the fault plane, giving rise to a semiconductorlike temperature dependence in conjunction with the thermal broadening effect of the Fermi level above 50 K. The curve fitting carried out on this basis has yielded satisfactory success in reproducing the experimental data over all the temperature ranges examined. The c-axis transport of carriers is undoubtedly related to the structural perfection of each specimen. However, it has to be noted that the so-called residual resistance ratio (r_R), defined as a conventional parameter based on the inplane transport data, does not necessarily give a direct measure of the stacking order of the basal planes, especially for those which are aligned almost in parallel. In fact, a HOPG with $r_R \sim 60$ was found to show higher values of ρ_c than those of the specimen with $r_R \sim 8.4$ in this study.

The pressure dependence of ρ_c has been elucidated in accordance with Noto and Tsuzuku,[12] who pointed out that it is roughly proportional to the dependence of the SW band parameters γ_1 and/or γ_2, resulting from an increase of the overlap of π wave function in the c direction. A comparison with the de Haas–van Alphen-effect

data has led to a conclusion that ρ_c at low temperatures is reduced by pressure about three times faster than at high temperatures. This is quite consistent with the fact that the peak of the temperature-dependence curve located near 50 K tends to collapse with increasing pressure.

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[1]W. Primak and L. H. Fuchs, Phys. Rev. **95**, 22 (1954).
[2]D. Z. Tsang and M. S. Dreseelhaus, Carbon **14**, 43 (1976).
[3]K. Kawamura, Y. Ouchi, H. Oshima, and T. Tsuzuku, J. Phys. Soc. Jpn. **46**, 578 (1979).
[4]G. L. Morgan and C. Uher, Philos. Mag. **46**, 427 (1981).
[5]J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958).
[6]S. Ono, J. Phys. Soc. Jpn. **40**, 498 (1976).
[7]K. Sugihara, Phys. Rev. B **37**, 4752 (1988).
[8]K. Sugihara, Phys. Rev. B **29**, 5872 (1984).
[9]S. Shimamura, Synth. Met. **12**, 365 (1985).
[10]R. Clarke and C. Uher, Adv. Phys. **33**, 469 (1984).
[11]R. G. Arkhipov, V. V. Kechin, A. I. Likhter, and Yu. A. Prospelov, Zh. Eksp. Teor. Fiz. **44**, 1964 (1963) [Sov. Phys.—JETP **17**, 1321 (1963)].
[12]K. Noto and T. Tsuzuku, J. Phys. Soc. Jpn. **35**, 1649 (1973).
[13]J. R. Anderson, W. J. O'Sullivan, J. E. Shirber, and D. E. Soule, Phys. Rev. **164**, 1038 (1967).