ESR of Material－Carbon

ESR can be used in research on carbon in the solid-state. E.g. the ESR spectrum of asymmetric Dysonian line shape [3] by conduction electron of pure single crystal graphite [1, 2] has been reported.

Graphite

Graphite is a hexagonal-plate crystal form of carbon. The planar structure is a turtle-shell-shaped graphene where carbons are connected by strong covalent bonds. Conversely, the layers are connected by weak Van der Waals' forces (Fig.1). Within the plane, electrical conductivity has metal-like properties, but semiconductor-like character is observed between planes. Graphite is used in many products including electric devices, automobiles, dry batteries, paint, etc.

Carbon nanotubes and fullerenes can be regarded as deformed graphenes. In addition, by injecting dopant between graphenes, conductivity can be improved or even develop superconductivity.

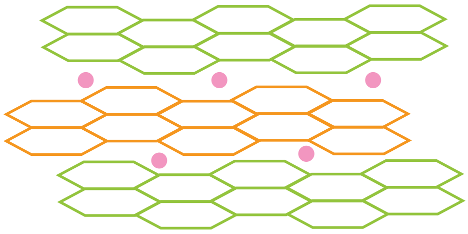

Fig 1. Basic Structure of Graphite

ESR Line Shape

Graphite and carbon fiber show a Dysonian absorption ESR line shape which is unique to conductive materials. Fig. 2 shows the ESR spectrum of a pencil lead. It is believed that the vertically asymmetric signal is observed because the microwave is affected by amplitude attenuation and the phase changes from the surface to the lower planes. When the size of sample particle or film thickness is less than the plane thickness, or when the diffusion time is long and the conductivity is low, this kind of distortion does not occur. From the ratio of A to B (Fig. 2), the time required for the conduction electrons to go through the plane can be obtained [4].

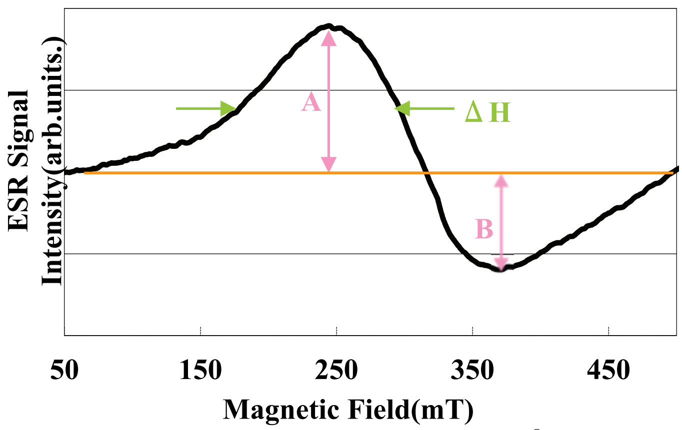

Fig 2. ESR Spectrum of Pencil Lead (200 ^{O}C)

The g-value and line width (ΔH), theoretical analysis has been conducted based on the electronic structure of graphite [5].

Copyright © 2011 JEOL Resonance Inc.

Conduction in Pencil Lead

Pencil lead (4B) was set in a test tube and its ESR spectrum was measured whilst the temperature was raised from −100 $^{\circ}$C to ＋200 $^{\circ}$C (ES-DVT4 was used). As the temperature of the graphite changes, the line width of the ESR spectrum also changes. At low temperature the signal position shifts to lower field (Fig 3). The large shift of the g-value and the increase of line width are characteristic of graphite, and they reflect the band structure near the Fermi potential[2].

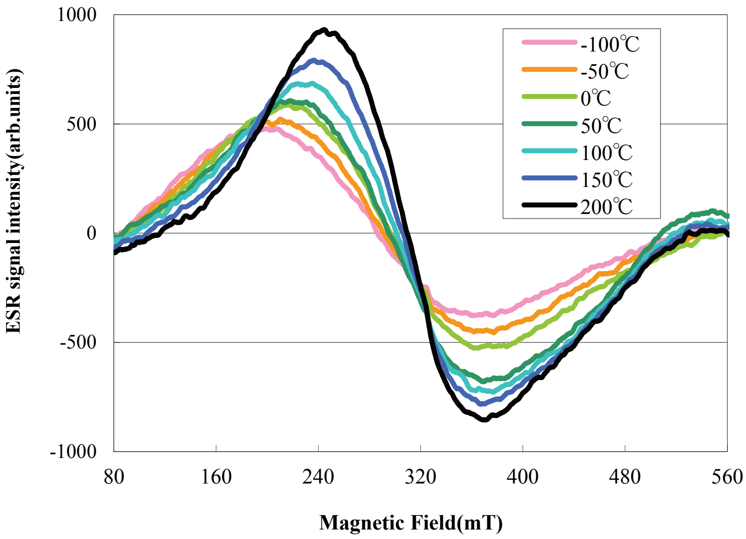

Fig. 3 ESR Spectra of Pencil Lead

ESR of Graphite：Characteristics of Changes at Low Temperature

- ○Signal intensity(number of spins) —— Pauli Paramagnetism + Semi-metallic property
- ○g-value shift —— Change of Fermi potential
- ○Increase of line width —— Overlapping of different Fermi potentials

ESR of Carbon

ESR is an important method in evaluating the solid-state properties of materials such as graphite as it gives information on electronic structure and conformation. The existence of Fullerene C_{60} was shown in 1985[6] and is basically diamagnetic, but it generates unpaired electrons as it is easily oxidized or reduced to form a radical. The electronic structure and solid-state property of endohedral Fullerenes have been studied [7,8,9]. The ESRs of carbon fiber and multi-layer carbon nanotubes are similar to those of poly-crystalline graphite, and are observed as overlapped signals of different g-values because of conduction electron and defects. [10]

Cited Literature

1) G.Wagoner (1960): Spin Resonance of Charge Carriers in Graphite, Physical Review, ***118***, 647-653.
2) H. Ohya and J, Yamauchi(1989): Electron Spin Resonance−Micro Characterization of Material−, Kodansha Scientific, p289.
3) F. J. Dyson (1955): Electron Spin Resonance Absorption in Metals. II. Theory of Electron Diffusion and the Skin Effect, Physical Review, ***98***, 349–359.
4) G.Feher and A.Kip (1955): Electron Spin Resonance Absorption in Metals. I. Experimental, Physical Review, ***98***, 337-348.
5) J.W. McClure and Y.Yafet(1961): Proc. Of 5th Conferemce of Carbon, ed. S.Mrozowski,M.L. Studebaker, P.L.Jr.Walker, University Park, PA, Pergamon Press,p22(1963).
6) H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley (1985): C_{60}: Buckminsterfullerene, Nature, ***318***, 162-163.
7) H. Shinohara, Y. Saito(1996):Chemistry and Physics of Fullerene, The University of Nagoya Univ. Press, p302.
8) C.C Chancey, M.C.M. O'Brien (1997): The Jahn-Teller Effect in C_{60} and Other Icosahedral Complexes, Princeton University Press.
9) The Chemical Society of Japan (Ed) (1999):Chemistry of Fullerene—The Third Isotope of Carbon—,Quarterly Kagakusosetu, ***43***, Japan Scientific Societies Press.
10) J.B.Jones and L.S.Singer (1982): Electron spin resonance and the structure of carbon fibers, Carbon, ***20***, Issue 5, p379-385.

Copyright © 2011 JEOL Resonance Inc.