

# Critical phenomena in quasi-2D intercalated graphite compounds $C_{24n} \cdot HSO_4^- \cdot 2H_2SO_4$ in a microwave field

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ESR measurements reveal a change in the state of conduction electrons in intercalated compounds of graphite when a threshold value of the microwave power ( $W$ ) incident on the sample is reached. The results also show that  $W$  affects the region and the nature of the critical temperature-induced transformation of the ESR spectrum.

The intercalation of graphite—the penetration of foreign atoms or molecules into the space between layers—results in anomalous changes in the properties of the graphite and also in the appearance of some fundamentally new properties.<sup>1</sup> In the present letter we report the observation of, and the results of a study of a critical temperature-induced change in the ESR spectrum of samples of a quasi-2D intercalated compound of graphite with the composition  $C_{24n} \cdot HSO_4^- \cdot 2H_2SO_4$  in the first ( $n = 1$ ) and second ( $n = 2$ ) stages of the intrusion. These effects have not been observed previously in an intercalated compound of graphite. The nature and region of the critical temperature-induced change in the ESR spectrum depend on the power of the microwave field at the sample. We have also observed a recovery of the phase of the intercalated graphite compound to a metastable value below the transition temperature upon the attainment of a threshold value of  $W$ .

Samples of the compound with  $n = 1$  and 2 are synthesized by the oxidation of highly oriented pyrolytic graphite in a sulfuric acid medium by fuming sulfuric acid ( $SO_3$ ) and nitric acid ( $HNO_3$ ). According to x-ray structural data, the distance between the carbon planes, which is  $3.35 \pm 0.01 \text{ \AA}$  in the initial highly oriented pyrolytic graphite, increases upon intercalation to  $7.88 \pm 0.05 \text{ \AA}$  ( $n = 2$ ) and  $8.01 \pm 0.05 \text{ \AA}$  ( $n = 1$ ). The ESR measurements were carried out in the  $Q$  band on an RE-1308 spectrometer. We use a  $H_{011}$  cylindrical resonator with a 100-kHz modulation of the static magnetic field  $H$ . The test samples have dimensions  $\sim 2 \times 1 \text{ mm}^2$  with a thickness  $\sim 0.3 \text{ mm}$ . The thicknesses of the skin layer of the compounds studied are  $\sim 8 \times 10^2 \text{ \AA}$  and  $\sim 3 \times 10^5 \text{ \AA}$  for the cases in which the microwave field  $\tilde{H}$  is, respectively, parallel and perpendicular to the carbon layers, according to calculations based on data on the electrical conductivity of these samples.<sup>2,3</sup>

At room temperature, we observe a single ESR signal from the initial graphite, from  $\pi$  conduction electrons, with a Dyson lineshape, as is characteristic of conducting samples. There is an axial (with respect to the  $c$  axis, perpendicular to the carbon layers) angular dependence of the position of the signal, with  $g_{\parallel} = 2.0474 \pm 0.0001$ , and with  $\Delta g = g_{\parallel} - g_{\perp} = 0.0445 \pm 0.0002$ . The line asymmetry parameter  $A/B$  depends on the orientation of the graphite with respect to  $H$  and  $\tilde{H}$ , but in all cases it is greater than 2.7. The widths at half-maximum of the low-field wing of the line,  $\Delta H_{1/2}$ ,

are  $0.09mT$  and  $0.43mT$  for the cases  $\mathbf{H} \parallel$  and  $\perp \mathbf{c}$  ( $\tilde{\mathbf{H}} \perp \mathbf{c}$ ), respectively. As the temperature is raised,  $A/B$ ,  $\Delta H_{1/2}$ , and  $\Delta g$  all decrease, the latter at a rate  $\sim 1 \times 10^{-4} \text{ deg}^{-1}$ . We observed no  $W$  dependence of the parameters of the lineshape or of the angular dependence of the spectrum.

The ESR spectra of both stages of the compound at 300 K and at values of  $W$  below a certain critical value  $W_0^+$  also consist of a single line. In terms of the symmetry of the spectrum and the lineshape, they are qualitatively the same as the ESR spectrum of the original highly oriented pyrolytic graphite. The parameters of the spectrum and of the lineshape determined for the case  $\tilde{\mathbf{H}} \perp \mathbf{c}$  for the various stages of the compound are equal to each other within the experimental errors, having the value  $g_{\parallel} = 2.0021 \pm 0.0001$ , with  $\Delta g = -0.0005 \pm 0.0001$ ,  $A/B \cong 4$ , and  $\Delta H_{1/2} \cong 0.036mT$ .

When the power of the microwave field applied to the resonator is attenuated below a certain critical value  $W_0^-$  ( $W_0^- < W_0^+$ ), the signal of the compound described above abruptly disappears. A new spectrum appears, also abruptly, consisting of two incompletely resolved lines of Dyson shape (Fig. 1). The parameters of the spectrum and of the lineshape (1 and 2 in Fig. 1) found for the two stages of the compound with  $\tilde{\mathbf{H}} \perp \mathbf{c}$ , are  $\Delta H_{1/2}(1) = 0.026mT$ ,  $\Delta H_{1/2}(2) = 0.024mT$ ,  $\Delta g(1-2) = g_{\parallel}(1) - g_{\parallel}(2) \cong g_1(1) - g_1(2) = 6 \times 10^{-5}$ , and  $A/B(1) > A/B(2) > 2.7$ .

In the stage of the compound characterized by a single Dyson line (stage  $\Phi_1$ ), with  $W < W_0^+$ , a brief cutoff of the microwave power from the resonator (for a time  $\Delta T < 10^{-2} \text{ s}$ ), which does not disrupt the tuning of the microwave circuit, restores the material to the stage characterized by two Dyson lines (stage  $\Phi_2$ ). The magnitude of the hysteresis,  $\Delta W = W_0^+ - W_0^-$ , does not depend on the index of the transition that is occurring,  $\Phi_1 \rightleftharpoons \Phi_2$ . As  $W \rightarrow W_0^+$  from the low-power side, we observe a splitting of the high-field line in the immediate vicinity of the transition  $\Phi_2 \rightarrow \Phi_1$ , an increase in the total breadth of the spectrum, and an increase by nearly an order of magnitude in the noise level on the signal (Fig. 1). For arbitrary orientations of  $\mathbf{H}$  and  $\tilde{\mathbf{H}}$  with respect to the compound, the spectral line corresponding to stage  $\Phi_1$  appears at approximately the same fields as does the average of the spectral components of the stage

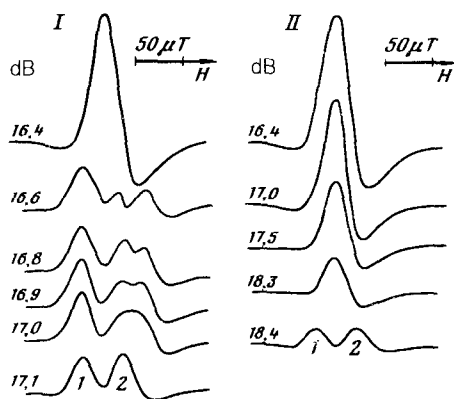


FIG. 1. Changes in the shape of the ESR spectrum of the intercalated graphite compound  $C_{24n} \cdot HSO_4^- \cdot 2H_2SO_4$  as the power  $W$  is (1) increased and (2) decreased.  $T = 300 \text{ K}$ ,  $\nu \cong 37 \text{ GHz}$ ,  $\mathbf{c} \parallel \mathbf{H}$ ,  $\perp \tilde{\mathbf{H}}$ .

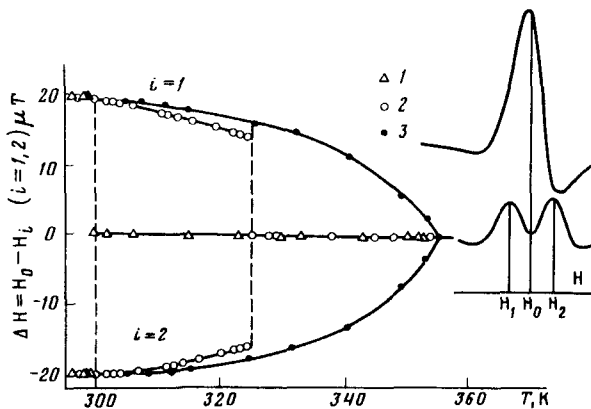


FIG. 2. Region and nature of the critical temperature-induced transformation of the ESR spectrum of the intercalated graphite compound  $C_{24n} \cdot HSO_4 \cdot 2H_2SO_4$ ,  $\Phi_2 \rightarrow \Phi_1$ , for various values of  $W$ : 1—15.5 dB; 2—17.5 dB; 3—18 dB ( $\nu \approx 37$  GHz,  $c \parallel H, \perp \bar{H}$ ).

$\Phi_2$  at power levels in the pretransition region, i.e., roughly between the outermost lines of this spectrum. As  $W \rightarrow W_0^-$  from the high-power side, we observe no pretransition changes in the spectrum.

As the test compounds are heated, they undergo a reversible temperature-induced transition  $\Phi_2 \rightarrow \Phi_1$ . The transition temperature  $T_0$  depends on  $W$ , becoming higher as the power is attenuated. At the same time, the nature of the change in the spectrum at temperatures in the critical region transforms from a clearly defined jump to a smooth coalescence of the lines, within the resolution of the instrument (Fig. 2). As the temperature is raised,  $\Delta W$  falls off.

We observed these critical changes in the ESR spectrum in both stages of the compound, in all the samples studied, including samples synthesized in different lots, and for all orientations of the compound with respect to  $H$  and  $\bar{H}$ .

A possible explanation for the instability which we have observed in the electronic structure of the compound with respect to changes in  $W$  and  $T$  is a Peierls instability accompanied by the formation of a charge density wave. This wave would result from changes in the electronic structure, especially of the valence band, and in the dynamic characteristics of the graphite during the intercalation of sulfuric acid molecules in it.

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<sup>1</sup>M. S. Dresselhaus and G. Dresselhaus, *Adv. Phys.* **30**, 140 (1981).

<sup>2</sup>E. McRae, D. Billand, J. F. Mareche, and A. Herold, *Physica* **B99**, 489 (1980).

<sup>3</sup>A. R. Ubbelohde, *Proc. Roy. Soc.* **321**, 445 (1972).

Translated by Dave Parsons