Diffusion and Phononlike Excitations in Intercalated Graphite from ^{133}Cs NMR and Relaxation

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The in-plane structure and dynamics of the intercalant Cs layer in CsC_{24} has been studied by ^{133}Cs quadrupole-perturbed NMR spectra and quadrupolar spin-lattice relaxation. The results show that the dominant excitations leading to the disordering of the mixed commensurate-incommensurate structure are phononlike shear modes interrupted by diffusion and displaying softening as the temperature approaches the deintercalation temperature.

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There have been many recent theoretical and experimental studies of alkali-metal layers intercalated in graphite, motivated by an interest in the collective dynamical behavior of two-dimensional (2D) model systems perturbed by a periodic lattice potential.[1] In particular, in the stage-2 graphite intercalation compound (GIC) CsC_{24}, diffraction studies have suggested a model of the in-plane Cs structure wherein the Cs atoms are arranged in $(\sqrt{7}\times\sqrt{7})$-$R19.11°$ superlattice registered regions separated by domains or discommensurations with honeycomb structure.[2–4] An open question of primary interest regards the dynamics driving the disordering within the intercalant layer in the high-temperature region. From quasielastic[5] and inelastic[6] neutron scattering and from Raman spectroscopy[7] there is evidence for the coexistence of planar liquidlike diffusive motion and acoustic and optical phonon branches including low-frequency shear modes. Since these motions should have distinctly different effects on the Cs quadrupole-perturbed NMR spectrum and quadrupolar spin-lattice relaxation, we have undertaken a study of these quantities to single out the dominant fundamental excitations and their role in the disordering mechanism.

In this paper we present data which can be interpreted in terms of the softening, on increasing temperature, of a low-frequency shear mode. This mode should correspond to rigid in-plane vibrations of Cs ions arranged in registered superlattice clusters whereby a correlated diffusion process, already noticed in neutron scattering,[5] limits its lifetime.

The measurements were performed in two highly oriented pyrolytic graphite (HOPG) samples, stage 2 (CsC_{24}), already used for neutron scattering (kindly provided by W. A. Kamitakahara).

The ^{133}Cs NMR quadrupole-perturbed spectra were obtained by Fourier transformation of the free-induction decay. The angular dependence of the spectra were studied by varying the angle θ between the external magnetic field and the normal to the carbon basal plane of the graphite. The ^{133}Cs spectrum ($2I=7$ components) is shown in Fig. 1 together with the angular dependence of the second-order shift of the central line (transitions are $\pm\frac{1}{2}\leftrightarrow\mp\frac{1}{2}$). For an electric field gradient (EFG) of cylindrical symmetry, the separation between two successive spectral lines is $(\nu_Q/2)(3\cos^2\theta-1)$, where $\nu_Q=3eQV_{zz}(1-\gamma_\infty)/14h$ is the quadrupole coupling constant, with Q the nuclear quadrupole moment, V_{zz} the EFG component along the symmetry axis, and γ_∞ the antishielding factor. One obtains $\nu_Q=80$ kHz, in agreement with the angular dependence of the second-order shift. This value is practically constant from 600 to 200 K, while it decreases to about 75 kHz at 4.2 K. Unexpectedly

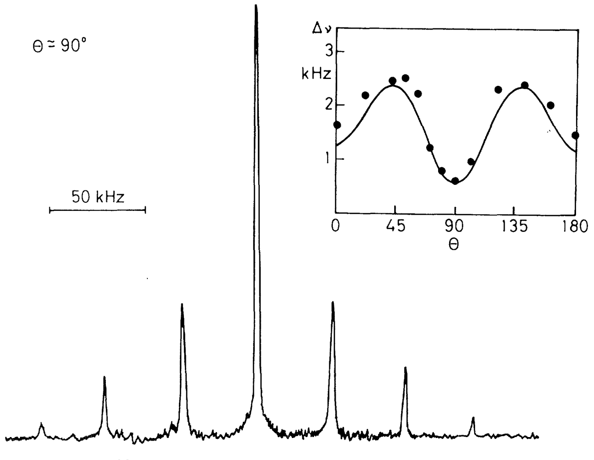

FIG. 1. ^{133}Cs quadrupole-perturbed NMR spectrum in CsC_{24} at $T\simeq300$ K and $\nu_L=9$ MHz. The angle between the normal to the basal plane and the external magnetic field is $\theta=\pi/2$. In the inset the angular dependence of the second-order shift of the central line is shown (solid circles, experimental results; solid line, theoretical angular dependence for $\nu_Q=80$ kHz and $\eta=0$ and for an isotropic Knight shift of -0.015%).

and at variance with the observation in CsC_8,[8] the satellite lines disappear progressively as the crystal is rotated more than about ±10° from $\theta = \pi/2$. Furthermore, the intensity ratio between the central and the satellite lines is larger than the theoretical values[9] and a substantial loss of signal is observed above 400 K.

The ^{133}Cs nuclear spin-lattice relaxation rates T_1^{-1}, measured for $\theta \simeq 55°$, where a common spin temperature occurs, are reported in Fig. 2. Under these conditions $T_1^{-1} = (10/105)(W_1 + 4W_2)$, where W_1, W_2 are the $\Delta m = 1, 2$ quadrupolar relaxation transition probabilities. For $\theta \neq 55°$ the recovery of the nuclear magnetization is no longer exponential and W_1, W_2 are strongly angle dependent, as expected for anisotropic motion. The details of these and other NMR effects will be reported elsewhere since they are not relevant for the subsequent discussion. In the following we will assume $W_1 \simeq W_2 = W$ and $T_1^{-1} \simeq W/2$.

The results for low temperatures ($T < 100$ K) (not shown in Fig. 2) are in agreement with previous measurements in powder samples[10] (provided that one takes into account the angular dependence of $W_{1,2}$ and of the recovery law) and indicate that the magnetic Korringa relaxation mechanism is completely negligible above ~10 K. One may note that at the so-called layer melting temperature[2] ($T_c \simeq 165$ K), no appreciable anomaly is present in the relaxation rate, indicating that the loss of long-range order does not affect the local dynamics.

The relevant experimental findings are as follows: (i) T_1^{-1} is anomalously large, increases strongly with temperature, and is frequency independent (fast-motion regime). (ii) A static quadrupole coupling is present, with ν_Q practically T independent, although fast temperature-dependent motions occur. (iii) The satelite lines are inhomogeneously broadened for $\theta \neq 55°$.

For a spin-lattice relaxation mechanism driven by the modulation of the EFG due to uncorrelated planar liquidlike diffusion one has[11] $T_1^{-1} \propto \tau_c$ where the only sizable temperature dependence comes from the diffusional correlation time $\tau_c \simeq a^2/D$. With use of $\tau_c^{-1} \sim \Delta\omega = 2Dq^2/S(q)$, where $\Delta\omega$ is the width of the quasielastic peak in Ref. 5, one obtains a temperature dependence of T_1 *opposite* to the experimental behavior.

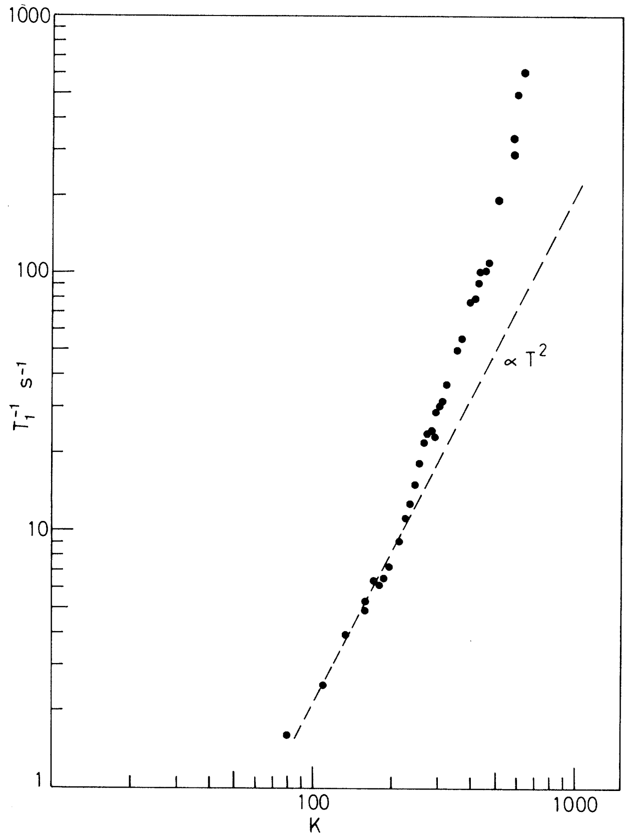

FIG. 2. Log-log plot of ^{133}Cs quadrupolar spin-lattice relaxation rate T_1^{-1} vs T in CsC_{24} for $\theta \simeq 55°$ at the measuring frequency $\nu_L = 9$ MHz. No appreciable frequency dependence was observed for $\nu_L = 13$ and 28 MHz, at room temperature.

Lattice vibrations normally drive the quadrupolar relaxation in insulators via a Raman two-photon process, yielding,[12,13] at high temperature, $T_1^{-1} \propto T^2$. The relaxation process is very sensitive to the phonon frequencies, suggesting that the anomalously short T_1 measured in CsC_{24} (compared, e.g., with $T_1 \simeq 1000$ sec in CsCl) should be related to the presence of the low-frequency shear resonant modes recently observed[6,7] in a stage-2 GIC. To embody in the theory the effect of diffusion we generalize the theoretical treatment for the relaxation due to optical modes[14] by considering a spread of the frequencies associated with the limitation of the phonon lifetime due to the diffusion. We obtain

$$W_{1,2} = \frac{e^2Q^2}{294}\frac{2\pi}{\hbar^2}\int \frac{\hbar^2}{m^2\omega^2} n_\omega(n_\omega+1)\, g(\omega)\, \delta(\omega-\omega_E) \left(\frac{\partial^2 V_{1,2}}{\partial u^2}\right)^2 d\omega, \qquad (1)$$

where the EFG functions $V_{1,2}$ have been expanded up to second order in the atomic displacement, with

$u^2 = n_\omega \hbar/m\omega$. The normalized distribution function $g(\omega)$ describing the density of phonon states for a dispersionless mode is approximated by a Lorentzian of width Γ centered at ω_E, where ω_E is an effective Einstein frequency describing the shear in-plane vibration of Cs clusters against the two carbon bounding layers and Γ is an inverse lifetime related to the planar diffusion.

The second derivatives have been evaluated numerically for a rigid shear motion, yielding

$$\partial^2 V_{1,2}/\partial u^2 \simeq \partial^2 V_{zz}/\partial u^2 = 0.2e(1-\gamma_\infty)C_0^{-5},$$

where $C_0 = 1.42$ Å is the C-C distance. From Eq. (1) one obtains ($Q = 0.04$ cm^2; $1-\gamma_\infty = 100$)

$$T_1^{-1} \simeq 7\times10^{34}\left(\frac{k}{\hbar}\right)^2 \frac{T^2}{\omega_E^4}\,\frac{1}{\Gamma}. \tag{2}$$

From neutron scattering results[5] one has for the reciprocal of the diffusional correlation time at room temperature $\tau_c^{-1} \sim \Delta\omega \simeq 3\times10^{11}$ rad/sec. Then from Eq. (2) we infer $\omega_E \simeq 10$ cm^{-1} which is of the same order of magnitude as found in Raman scattering.[7]

Since the alternative relaxation possibilities examined here, namely, the Korringa mechanism, simple diffusion, and normal phonon modes, yield the wrong order of magnitude and/or the wrong temperature dependence we argue that the low-frequency shear modes, considered above, with a lifetime of the order of the diffusional correlation time, $\Gamma^{-1} \sim \Delta\omega^{-1}$, are responsible for the relaxation rate. Furthermore, the data in Fig. 2 show that for $T > 200$ K the relaxation rate increases faster than T^2. This effect can be attributed to a temperature dependence of ω_E.[13] The behavior of ω_E vs T derived from Eq. (2) and the experimental data for T_1 in Fig. 2 are shown in Fig. 3. While the absolute value of ω_E is only indicative, its relative temperature dependence is not affected by the crudeness of the evaluation of the magnitude of the relaxation rate. In deriving the values of ω_E we have assumed a temperature independent $\Gamma \sim \Delta\omega$. The softening of the effective frequency ω_E is even more pronounced if one allows for the temperature dependence of Γ (see Fig. 3).

This interpretation provides new insights into the dynamics driving the disordering of the Cs ions when the deintercalation temperature is approached, the behavior of T_1^{-1} bearing a resemblance to the critical behavior observed at phase transitions.[15]

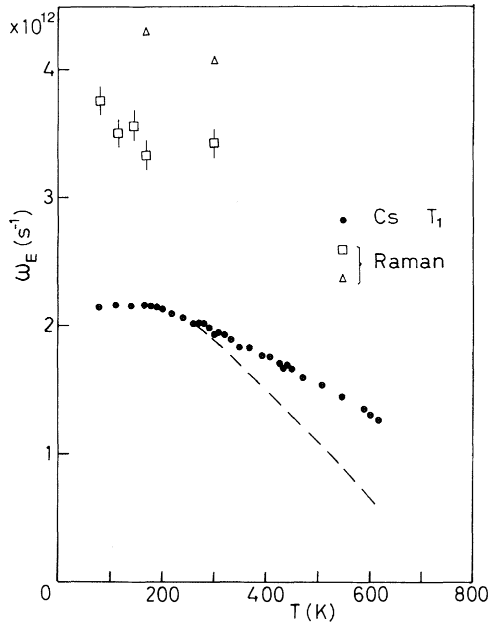

FIG. 3. Temperature dependence of the frequency ω_E derived from Eq. (2) and the data of T_1^{-1} in Fig. 2. The lowest frequencies obtained from Raman scattering (Ref. 7) are shown for comparison. The dashed line represents the behavior that one would obtain for ω_E if the temperature dependence of Γ in Eq. (2) were taken into account according to the experimental data in Ref. 5. The deintercalation temperature in CsC$_{24}$ is around 640 K.

The interpretation of the quadrupole-perturbed spectrum and of its angular dependence in terms of the strength and the local distribution of the EFG tensor requires a detailed evaluation of the different sources of EFG. Here we present only the conclusions of such an analysis. The measured value of $\nu_Q = 80$ kHz is well reproduced by evaluating the EFG with the usual separation into a conduction-electron contribution and an ionic contribution. The first contribution is zero for a uniform charge distribution localized on the bounding carbon layers while the leading ionic term comes from the Cs ions within the intercalant plane. The mixed commensurate-incommensurate in-plane structure produced a local modulation of the first-order quadrupole shift which is responsible for the anomalies in the rotation pattern observed in CsC$_{24}$ but not in CsC$_8$ where the satellite lines could be observed at all angles.[8] The planar liquidlike diffusion does not average out these effects because it involves, in our picture, a collective motion of Cs ions which retain the local correlated superlattice structure.

In summary, we argue that our ^{133}Cs NMR data prove that in CsC$_{24}$ the dominant collective excitations of the intercalant are phononlike low-frequency modes coupled with liquidlike floating diffusion. This picture complements and specializes the one provided by neutron scattering data.[5]

Furthermore, the data indicate that these large-amplitude, low-frequency, short-lifetime excitations exhibit a slowing down with increasing temperature, thus driving the disordering process.

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