

# Knight shift and inhomogeneous distribution of the spin density in the quasi-one-dimensional disordered conductor $\text{Qn}(\text{TCNQ})_2$

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The high-resolution NMR spectrum and the relaxation of carbon-13 nuclei in  $\text{Qn}(\text{TCNQ})_2$  have been studied. The results reveal a broadening, caused by a structural disorder, of a line with a Knight shift. The distribution function of the electron spin density has been measured. The spin density varies by a factor of five at the various TCNQ molecules.

1. The complex of TCNQ with quinoline,  $\text{Qn}(\text{TCNQ})_2$ , is one of the conducting salts of TCNQ which exhibit a structural disorder due to a random orientation of asymmetric cations.<sup>1</sup> The role played by the disorder in these systems in their metallic phase has been discussed primarily on the basis of data on the temperature and frequency dependence of the complex admittance,<sup>2,3</sup> which has been described successfully<sup>4</sup> by a theory which incorporates the joint effects of a disorder and of phonons on the one-dimensional localization of electrons. However, there has been no direct experimental evidence of an effect of structural disorder on electronic states. We have now extracted such information from measurements of the Knight shifts in the high-resolution NMR spectra of carbon-13. We find that a structural disorder causes an inhomogeneous distribution of the electron spin density over the TCNQ chains. High-resolution measurements are necessary because the line broadening due to internuclear interactions is comparable to the Knight shift and also because of an anisotropy of the shifts (chemical and Knight), which would make it impossible to observe the effects of interest here in the NMR of broad lines.

2. The present measurements are carried out on a Bruker CXP-200 pulsed spectrometer in a 47-kG magnetic field at room temperature. The high resolution is achieved by cross-relaxation methods with proton decoupling and by means of a rapid rotation of the sample, at 4–5 kHz, through the magic angle; these techniques cause the dipole–dipole interaction of the nuclei and the anisotropy of the chemical and Knight shifts to average out to zero. The spin-lattice relaxation time  $T_1$  and the spin-spin relaxation time  $T_2$  are measured under high-resolution conditions by  $180^\circ\text{-}\tau\text{-}90^\circ$  and  $90^\circ\text{-}\tau\text{-}180^\circ\text{-}\tau$  pulse sequences. We use polycrystalline  $\text{Qn}(\text{TCNQ})_2$  samples enriched to a 40% concentration of the isotope  $^{13}\text{C}$  in the TCNQ cyan groups. For comparison, we study the structurally ordered complex TTF-TCNQ (TTF is tetrathiofulvalene), for which enrichment was not required since the NMR lines are narrow. The Knight shifts are measured from the  $^{13}\text{C}$  line of the cyan group of neutral TCNQ (112.6 ppm on the standard tetramethylsilane scale).

3. For both of the complexes studied we observe the diamagnetic Knight shift of the line of the TCNQ cyan group that has been seen previously<sup>5,6</sup> (Fig. 1). An impor-

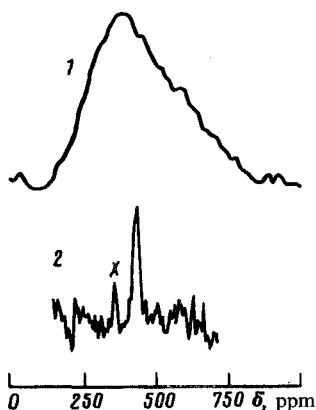


FIG. 1. High-resolution NMR spectra of  $^{13}\text{C}$  of the cyan group of (1)  $\text{Qn}(\text{TCNQ})_2$  and (2) TTF-TCNQ. X—Side bands from rotation of the sample.

tant difference between the two spectra in the present study is a broadening of the  $\text{Qn}(\text{TCNQ})_2$  line which cannot be attributed to paramagnetic impurities or structural defects, since a recrystallization in acetonitrile does not alter the spectrum. The relaxation rates are different in different parts of the line, and the dependence of the relaxation rate on the shift  $\delta$  is described by  $T_1^{-1} = 3.6 \times 10^{-4} \delta^2 + 28 \text{ s}^{-1}$  and  $T_2^{-1} = 2.7 \times 10^{-3} \delta^2 + 445 \text{ s}^{-1}$  (Fig. 2). The constant contributions stem from relaxation mechanisms which are of no importance to the conclusions reached here and which will not be discussed. A similar quadratic dependence,  $T_1^{-1} \propto K^2$ , on the Knight shift  $K$  is characteristic of a Corringa relaxation, and it is reasonable to suggest that the broadening of the  $\text{Qn}(\text{TCNQ})_2$  line is caused by a distribution of Knight shifts. The homogeneous broadening, estimated from  $T_2^{-1}/\pi$ , does not exceed 12 ppm and constitutes a small fraction of the line width.

4. The distribution of Knight shifts is caused by the random potential of the disordered chain of  $\text{Qn}^+$  cations which causes an inhomogeneous distribution of the electron spin density at the TCNQ molecules. Denoting by  $f_x(x)$  the distribution function of the nonequilibrium values of the spin  $s$  at the molecules in the magnetic field  $H$ , and using the expression  $K = a\gamma_e s / \gamma_n H$  for the Knight shift, we can describe the

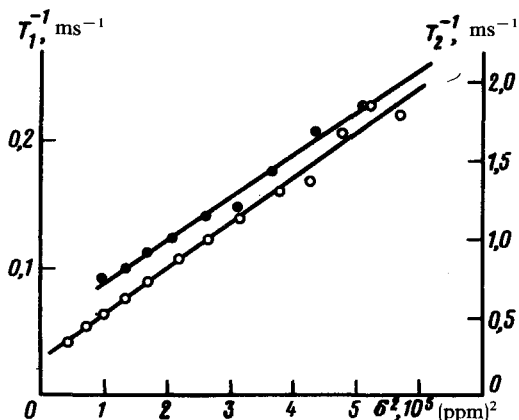


FIG. 2. The nuclear relaxation rate of  $\text{Qn}(\text{TCNQ})_2$  as a function of the shift  $\delta$ .  $\circ$ — $T_1^{-1}$ , scale at the left;  $\bullet$ — $T_2^{-1}$ , scale at the right; solid lines—approximations by the equations given in the text proper.

shape of the NMR line of an inhomogeneous chain by<sup>7</sup>  $g(\nu - \nu_0) = \int g_0(\nu - \nu_0 - a\gamma_e x) f_s(x) dx$ , where  $a$  is the constant of the isotropic hyperfine interaction,  $\gamma_e$  and  $\gamma_n$  are the gyromagnetic ratios of the electron and the nucleus, and  $g_0(\nu - \nu_0)$  is the shape of the line, whose center is at the frequency  $\nu_0$ , for a homogeneous diamagnetic ( $s=0$ ) chain. Since the homogeneous broadening is small, we can assume that the  $g(\nu - \nu_0)$  line is a sum of  $\delta$ -functions. In this case we would have  $g(\nu - \nu_0) = f_s[(\nu - \nu_0)/a\gamma_e]$ : The NMR lineshape reproduces the spin distribution function, and the observed range of Knight shifts, from 150 to 750 ppm, implies variations in the spin density at the different TCNQ molecules over a range amounting to a factor of five.

5. The Corringa relation predicts  $T_1^{-1} = T_2^{-1} = (4k/\hbar)(\gamma_n/\gamma_e)^2 TK^2 = 7.1 \times 10^{-5} K^2$  for the nucleus  $^{13}\text{C}$  at  $T = 293$  K. This prediction is well below the measured value of  $T_1^{-1}$  and is inconsistent with the observed values  $T_1^{-1} > T_1^{-1}$ . An acceleration of the spin-lattice relaxation in comparison with the Corringa prediction is a well-known effect for protons in TCNQ complexes and is a consequence of a one-dimensional diffusive motion of electron spins.<sup>8,9</sup> We must therefore use the more general expression<sup>9</sup>

$$T_1^{-1} = (\hbar\gamma_e\gamma_n N/\chi)^2 \left[ \frac{3}{5} \epsilon F_0 + \left(1 + \frac{7}{5} \epsilon\right) F_1 \right] K^2,$$

which, as can be shown, is also valid in the case of an inhomogeneous system. Here  $\chi$  is the molar electron paramagnetic susceptibility,  $N$  is the number of TCNQ molecules per mole,  $F_0$  and  $F_1$  are the spectral densities of the fluctuations of the electron spin at the nucleus at a zero frequency and at the electron Larmor frequency, respectively, and  $\epsilon = d^2/a^2$ , where  $d$  is the constant of the anisotropic hyperfine interaction. Using<sup>1</sup>  $\chi = 4.7 \times 10^{-4}$  cm<sup>3</sup>/mole for Qn(TCNQ)<sub>2</sub> at  $T = 293$  K, and taking the values  $F_0 = 1.3 \times 10^{-6}$  s and  $F_1 = 7.25 \times 10^{-8}$  s from measurements of proton relaxation,<sup>9</sup> we find  $T_1^{-1} = (3.51 + 42.5\epsilon) \times 10^{-4} K^2$ . Although we do not know the value of  $\epsilon$ , an agreement with experiment can be reached by choosing the physically reasonable value  $\epsilon \approx 0.002$ , which would indicate that the anisotropic hyperfine interaction is of minor importance. According to the theory of nuclear relaxation, we would have  $T_1/T_2 = (F_0 + F_1)/2F_1 = 9.4$ , which would explain the observed values  $T_2^{-1} > T_1^{-1}$  and which would agree with the measured ratio  $T_1/T_2 = 7.5$ .

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<sup>1</sup>I. F. Shegolev, Phys. Status Solidi **a12**, 9 (1972).

<sup>2</sup>A. N. Bloch, R. B. Weisman, and C. M. Varma, Phys. Rev. Lett. **28**, 753 (1972).

<sup>3</sup>G. Grüner, Chemica Scripta **17**, 207 (1981).

<sup>4</sup>A. A. Goglin, S. P. Zolotukhin, V. I. Mel'nikov, É. I. Rashba, and I. F. Shegolev, Pis'ma Zh. Eksp. Teor. Fiz. **22**, 564 (1975) [JETP Lett. **22**, 278 (1975)].

<sup>5</sup>E. F. Rybaczewski, L. S. Smith, A. F. Garito, A. J. Heeger, and B. G. Silbernagel, Phys. Rev. B **14**, 2746 (1976).

<sup>6</sup>E. Lippmaa, M. Alla, H. Raude, R. Teeäär, I. Heinmaa, and E. Kindla, Magnetic Resonance and Related Phenomena (ed. E. Kindla, E. Lippmaa, and T. Saluvere), Springer-Verlag, New York, 1979, p. 87.

<sup>7</sup>L. N. Bulaevskii, Zh. Eksp. Teor. Fiz. **75**, 748 (1978) [Sov. Phys. JETP **48**, 377 (1978)].

<sup>8</sup>G. Soda, D. Jerome, M. Weger, J. Alizon, J. Gallice, H. Robert, J. M. Fabre, and L. Giral, *J. Phys. (Paris)* **38**, 931 (1977).

<sup>9</sup>F. Deyreux and M. Nechtschein, *Lecture Notes in Physics* **95**, 145 (1979).

<sup>10</sup>C. P. Slichter, *Principles of Magnetic Resonance with Examples from Solid State Physics*, Harper and Row, New York (Russ. transl. Mir, Moscow, 1981).

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