

Neutron Scattering and the Electron-Phonon Coupling in One-Dimensional Conductors

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(Received 3 August 1976)

I suggest that the Kohn anomaly in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) occurs in C-H (or C-D) molecular modes rather than in an acoustic phonon. Structure-factor calculations explain why neutron-scattering results from protonated and deuterated samples are very different. A tentative identification of the involved modes is consistent with the TCNQ chains' ordering at $T=54$ K and the TTF chains' ordering at $T=47$ K. A similar analysis of $K_2[Pt(CN)_4]Br_{0.3} \cdot 3.2D_2O$ verifies that the anomaly occurs in the longitudinal acoustic phonon.

In a recent neutron inelastic-scattering study from tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), Mook and Watson¹ reported the observation of a giant Kohn anomaly at room temperature, which they associated with the longitudinal acoustic phonon propagating parallel to the chain direction of the molecules. In a similar study from a fully deuterated compound, Shirane *et al.*² reported quite different observations on the basis of which they concluded that the Kohn anomaly occurred only at low temperatures and appeared to be primarily associated with the transverse acoustic phonon. In this Letter, I suggest that the electron-phonon coupling in TTF-TCNQ is such that the phonon anomaly occurs in the C-H (or C-D) molecular modes. My calculations of neutron intensities for such modes are capable of explaining large differences between results from protonated TTF-TCNQ (H) and deuterated TTF-TCNQ (D); and I use the experiments to make a tentative identification of the relevant modes on both the TTF and the TCNQ molecules. While conclusive evidence will have to await new experiments, I shall conjecture how my analysis may yield a microscopic understanding of the electron-phonon coupling, which appears consistent with the present picture of the structural changes³⁻⁵ as well as recent explanations of the resistivity of TTF-TCNQ.⁶ A brief analysis of the extensively studied $K_2Pt(CN)_4Br_{0.3} \cdot 3.2D_2O$ (KCP) shows, as expected, that the anomaly originates from the longitudinal acoustic phonon.^{7,8}

Consider a lattice normal mode, characterized by its frequencies $\omega(\vec{q})$ and the eigenvectors of unit length $\sigma_s(\vec{q})$ for each participating atom with position \vec{r}_s in the unit cell. Confining ourselves to "one-phonon creation," we find that the double differential cross section for neutron scattering

becomes⁹

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{(2\pi)^3}{V} \frac{k'}{k} \frac{n(\omega)+1}{m\omega} \sum_{\vec{q}} \delta[\omega - \omega(\vec{q})] \times \sum_{\vec{\tau}} \delta(\vec{Q} - \vec{q} - \vec{\tau}) |F(\vec{Q})|^2, \quad (1)$$

where \vec{k}' and \vec{k} are outgoing and incoming wave vectors of the neutron with mass m , $n(\omega) = [\exp(\hbar \times \omega/k_B T) - 1]^{-1}$, $\tau = \vec{Q} - \vec{q}$ is a reciprocal lattice vector, and V is the volume of the unit cell. In (1), the inelastic-neutron-scattering structure factor is given by

$$F(Q) = \sum_s b_s A_s^{-1/2} (\vec{Q} \cdot \vec{\sigma}_s) \times \exp[-2W_s(\vec{Q})] \exp(i\vec{Q} \cdot \vec{r}_s), \quad (2)$$

where b , A , and W_s denote neutron scattering length, mass number, and the Debye-Waller factor, respectively. In Table I, I show the scattering lengths as well as the coherent and incoherent cross sections for H, D, and C. Whereas the most prominent effect of deuteration is often considered to be the change in the incoherent scattering, the difference in sign of b between H and D can give rather drastic effects as well.

It is noteworthy that a measurement of $F(Q)$ is particularly simple in the case of a one-dimen-

TABLE I. Neutron cross sections and scattering lengths in TTF-TCNQ. [Data are taken from G. E. Bacon, *Neutron Diffraction* (Clarendon, Oxford, 1975).]

	b (10^{-12} cm)	σ_{COH} (b)	σ_{INC} (b)
H	-0.374	1.76	79.7
D	0.667	5.56	2.0
C	0.665	5.51	~0.0

sional conductor, for the lattice excitations associated with electron phonon coupling. Because of one dimensionality, at least to a good approximation $\omega(q)$ does not depend on the wave-vector component \vec{q}_\perp , perpendicular to the chain direction. This means that if I only vary \vec{q}_\perp , i.e., measure the intensities along a given " $2k_F$ plane," all the wave-vector dependence in (1) is contained in $F(\vec{Q})$. In KCP, Carneiro *et al.*⁷ performed such measurements. They measured the inelastic neutron intensity along a series of $2k_F$ planes, and found that it followed the one-dimensional elastic structure factor as calculated by Lynn *et al.*⁸

From this I can identify the scattering in the giant Kohn anomaly of KCP as associated with the longitudinal acoustic phonon propagating parallel to the chain, since the inelastic structure factor calculated according to (1) for this normal mode is virtually identical to the elastic structure factor. This identification shows that neutron scattering can serve as an important tool in the detailed investigation of the nature of the electron-phonon coupling in one-dimensional materials.

In TTF-TCNQ the situation is, as has been men-

tioned, not as well resolved as in KCP. I shall therefore investigate the alternative possibility that the $2k_F$ instability occurs in an optic mode; and as an example, I shall calculate the structure factors for the C-H (or C-D) bond stretching modes. Since the neutron scattering to which we want to compare our calculations was performed in a geometry where $\vec{Q} = (0, K, L) = K\vec{b}^* + L\vec{c}^*$ with \vec{b}^* pointing along the chain, I only consider the modes which contribute in this scattering geometry. These are shown in Figs. 1 and 2 together with the structure factors calculated according to (2). In computing $|F(\vec{Q})|^2$, I have treated the two molecules in the unit cell as independent (and also the two ends of the TTF molecule), and further neglected the Debye-Waller factor. The atomic positions were taken from the structural work of Kistenmacher, Phillips, and Cowan¹⁰ with the approximation that all C-C-H bond angles are 120° . The results of the calculations, also shown in Figs. 1 and 2, indicate that the neutron-scattering intensities from this type of modes should indeed be remarkably different in TTF-TCNQ (H) and TTF-TCNQ (D).

With the rather few experimental data available,

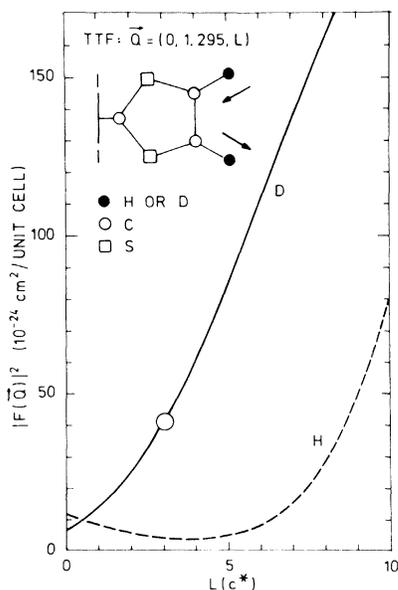


FIG. 1. Neutron intensities $|F(\vec{Q})|^2$, calculated according to (2) for a C-H (or C-D) bond stretching mode of the TTF molecules in TTF-TCNQ, when $\vec{Q} = (0, K, L)$. Arrows indicate simultaneous displacements of the protons (or deuterons) from this mode. The circle shows where my analysis suggests that the mode has been observed at low temperatures in TTF-TCNQ (D) by Shirane *et al.* (Ref. 2).

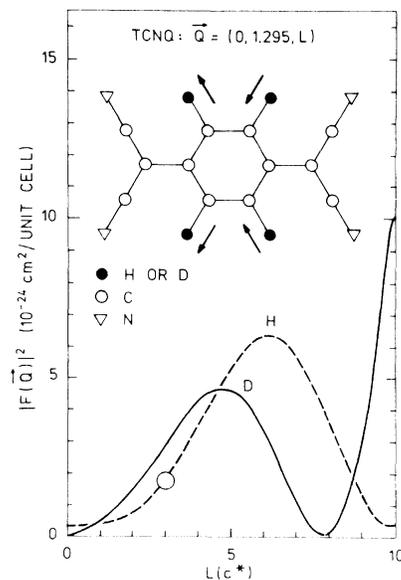


FIG. 2. Neutron intensities $|F(\vec{Q})|^2$, calculated according to (2) for the C-H (or C-D) bond stretching mode of the TCNQ molecules in TTF-TCNQ, when $\vec{Q} = (0, K, L)$. Arrows indicate simultaneous displacements of the protons (or deuterons) from this mode. The circle shows where my analysis suggests that the mode has been observed at room temperature in TTF-TCNQ (H) by Mook and Watson (Ref. 1). Note the change in scale between Figs. 1 and 2.

only a tentative identification of the soft phonons in TTF-TCNQ can be made. In TTF-TCNQ (D) Shirane *et al.*² observed the Kohn anomaly below $T = 120$ K at $\vec{Q} = (0, 1.295, 3)$. At room temperature an extensive search revealed no giant Kohn anomaly. Since the dominant scattering in my calculation comes from the TTF mode, I suggest that their measurements reflect a temperature-dependent coupling of the electronic excitations to the C-H or (C-D) modes of the TTF molecule. My structure factor increases with increasing L , so that the anomaly at low temperatures should be observable for $L > 3$; and my calculations predict that this should also be the case in several other $2k_F$ planes. It seems, therefore, worthwhile to repeat the extensive measurements at low temperatures, so far only done at room temperature. The structure factor for the observed TTF mode is 10 times larger than for the TCNQ mode. Therefore, I do not expect any information from the latter type of modes in TTF-TCNQ (D).

With this information gained from the deuterated compound, the scattering observed in TTF-TCNQ (H) at room temperature should come from the modes in the TCNQ molecule. The structure factor according to Fig. 2 is $|F(Q)|^2 = 2$, but since Mook and Watson¹ used a total volume of protonated crystals which was 10 times bigger than the deuterated ones used by Shirane *et al.*, the measured intensities scale approximately as indicated by our calculations.

The picture emerging from the above analysis is that at high temperatures the electron-phonon coupling softens the C-H (or C-D) modes of the TCNQ molecules in TTF-TCNQ. At lower temperatures, similar effects occur in the TTF molecules. Because of the dominance in TTF-TCNQ (D) of the TTF mode, an isolated study of the temperature dependence seems to be possible in this case, whereas it does not seem obvious how to isolate the TCNQ mode, and its temperature dependence in particular. But even with the very limited evidence so far available, it is satisfactory that my picture agrees well with a series of other experiments and suggestions. Analyzing the structural studies by Comès *et al.*,³ Bak and Emery⁴ showed that in TTF-TCNQ the three-dimensional ordering occurs separately on the two sets of chains at $T = 54$ and $T = 47$ K. This has been experimentally confirmed,⁵ but without a positive identification of which chain orders at which temperature. My analysis suggests that the ordering should occur on the TCNQ chains at 54 K, since

these chains show the soft phonon even at high temperatures, and then that the ordering on the TTF chains should occur at 47 K. Recent magnetic-susceptibility measurements¹¹ also indicate that the TCNQ molecules order at the higher temperature. Further support to this picture comes from the observation¹² that it is the lower transition which is the most sensitive when Se is gradually substituted for S or the TTF molecules, whereas the upper transition (on the TCNQ chains) is rather unchanged by this substitution. It is also possible to understand the results of diffuse x-ray scattering, reported independently by Kagoshima *et al.*¹³ and by Comès.¹⁴ Both groups find rather poorly defined diffuse streaks at room temperature, which become well defined and increase in intensity below $T = 150$ K. Since the modes I have considered are associated with light atoms, which do not scatter x rays appreciably, I expect well-defined diffuse x-ray scattering only at lower temperatures, when the TTF chains are distorted so much that it shows up in the scattering from the heavier sulfur.

The idea that the anomaly should occur in an optic mode rather than in an acoustic one has already been suggested by several authors. In particular, Weger, Horowitz, and Gutfreund⁶ have shown that it is easier to understand the temperature dependence of the resistivity if the frequency of the unperturbed mode ω_0 is large compared to the transition temperature. For the modes I have considered,¹⁵ I have $\omega_0(\text{C-H}) = 3050 \text{ cm}^{-1}$ and $\omega_0(\text{C-D}) = 2270 \text{ cm}^{-1}$; but other C-H and C-D modes can of course be involved. Two alternative mechanisms, responsible for the observed inelastic neutron scattering, have also been forwarded, however. Morawitz¹⁶ has shown that electron-libron interactions may be important, whereas Mook and Torrance¹⁷ have interpreted the scattering from TTF-TCNQ (H) in terms of spin waves. Since each mechanism has its characteristic inelastic structure factor, neutron experiments as outlined here should provide a means of distinguishing between the different mechanisms.

Besides the fact that I can explain differences in the neutron scattering results by invoking the C-H (C-D) modes in TTF-TCNQ as responsible for the Kohn anomaly, there is another interesting observation which favors these modes as candidates when compared with the numerous other molecular modes. By inspecting the structure,¹⁰ one finds that the molecular overlap of the TCNQ molecules is unique in that it appears to favor a

coupling between the C-H (C-D) molecular modes along the chain direction. This again is consistent with the particular importance of the TCNQ chains, and it appears that this observation may contain the microscopic reason for much of the behavior of TTF-TCNQ.

The author is indebted to his former colleagues at Brookhaven National Laboratory for initiating his interest in one-dimensional conductors. The communication of unpublished results from H. Mook and G. Shirane, and useful conversations with K. Bechgaard and O. Faurshov Nielsen are gratefully acknowledged.

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New Coherent Averaging Effect in Magnetic Resonance: Modulation-Induced Reduction of Dipolar Coupling

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(Received 19 July 1976)

Modulation was used in a transient nutation experiment to remove dipolar splitting. We calculate this new effect and demonstrate it for an isolated two-spin system. The relatively simple technique works efficiently for line narrowing in polycrystalline solids and preliminary results indicate that it should be useful for uncovering chemical-shift and heteronuclear-coupling information obscured by homonuclear broadening.

Modulation has been used extensively in NMR spectroscopy, especially for detection in solid-state experiments and for both detection and decoupling in liquid-state studies. Recently, there has been considerable interest in the effect of strong modulating fields on the Larmor frequency of spins in both optical and NMR experiments. The phenomenon of "photon dressing," in which the modulation frequency is much greater than the Larmor frequency, has been of particular interest.¹ In this communication, we report a new coherent averaging process in magnetic resonance which is effected by the use of modulation. By adjusting the modulation frequency and index, it is possible to reduce the homonuclear dipolar coupling among spins, suggesting a relatively

simple new technique for obtaining high-resolution NMR spectra in ordered media.

Consider a coupled two-spin system subjected to modulation of the static field H_0 as well as continuous rf irradiation at the center of the spectrum. The Hamiltonian viewed from a reference frame rotating with the frequency ω_0 of the resonant field is²

$$\mathcal{H} = -\omega_1(I_{x1} + I_{x2}) - \kappa\omega_M \cos\omega_M t (I_{z1} + I_{z2}) - A(3I_{z1}I_{z2} - \vec{I}_1 \cdot \vec{I}_2), \quad (1)$$

where $\omega_1 = \gamma H_1$, and $2H_1$ is the peak amplitude of the linearly polarized rf field. The first term represents the Zeeman interaction in the rotating frame and the last term is the truncated dipolar