$(T_1)^{-1} - (T_1^\infty)^{-1} = f(t)$ is shown in Fig. 2. The curves for different fields have the same shape and can be fitted to the curve at zero field by multiplying the time scale by a factor A. We define $A(H) = v_c(H)/v_c(0)$ as the relative conversion rate. The results are shown in Fig. 3. There is a sharp peak at 12.5 kOe, which corresponds to an electronic Zeeman splitting of 1.7°K. The error flags indicate the maximum deviation consistent with the data of Fig. 2. There seems to be a second peak at 15.2 kOe (2.05°K). It is tempting to speculate that the first peak corresponds to the sixfold level at ϵ_1 and the second to the triplet at ϵ_2. If such an assignment were true, the observed intensity ratio of 2 would indicate that the matrix element for transitions $T \to A$ is independent of the sublevel in the T manifold. In this case, the intensity ratio is expected to increase at lower temperatures because of depopulation of the higher level of the T manifold. Measurements down to 0.3°K are in preparation in this laboratory.

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Enhanced Nuclear Relaxation in a One-Dimensional Metal near the Mott Transition*

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We present an experimental study of the nuclear spin-lattice relaxation in a one-dimensional metal near the metal-insulator transition. The data obtained from the charge transfer salt N-methyl-phenazinium–tetracyanoquinodimethan directly confirm the enhanced susceptibility predicted for a one-dimensional metal at $q \simeq 2k_F$ and provide insight into the nature of the metal-insulator transition.

It is a well-known theoretical result that one-dimensional (1D) metals show, at $T = 0$°K, a singularity in the magnetic susceptibility $\chi(\vec{q}, \omega = 0)$ at $q = 2k_F$.[1] At finite temperature, as the Fermi surface is smeared, the singularity is removed leaving a peak in the response function (near $q = 2k_F$), the magnitude of which varies logarithmically with $E_F/k_B T$. The effect of the electron-electron (e-e) interaction in a 1D system is thus expected to be more important in the enhancement of $\chi(q \simeq 2k_F)$ than that of the uniform susceptibility $\chi(q = 0)$. In the random-phase approximation (RPA) the enhancement factor is given by $[1 - U_C(q)\chi_0(q, \omega)]^{-1}$, where $U_C(q)$ is the Fourier transform of the Coulomb interaction (reduced by Coulomb-hole correlations), and $\chi_0(q, \omega)$ is the independent-particle susceptibility.[2] As the temperature is lowered and $U_C(2k_F)\chi_0(2k_F, \omega)$ approaches unity, an instability should occur and a transition (e.g., to a magnetic Mott insulator) may take place. Measurable quantities (such as NMR relaxation) which depend upon $\chi(q, \omega)$ will be strongly enhanced near such a transition.

N-methyl-phenazinium–tetracyanoquinodimethan (NMP)(TCNQ) was recently shown[3] to possess a one-dimensional electronic structure, to be metallic above 200°K, and to exhibit a continuous transition from metal to small–band-gap

Mott insulator as the temperature is lowered below 200°K. Based on low-temperature specific-heat and susceptibility data, it was shown[3] that the ground state and low-lying excitations could be described by the 1D Hubbard model. Above 200°K, the conductivity, thermoelectric power, and temperature-independent spin susceptibility indicate a correlated metallic Fermi liquid.

We present here measurements of the nuclear spin-lattice relaxation time T_1 of (NMP)(TCNQ) and analyze the data in terms of the electronic correlation time τ_c. In the limit of very short τ_c, the relaxation can be written as $T_1^{-1} = \langle H^2 \rangle \tau_c$, where $\langle H^2 \rangle$ represents the "strength" of the interaction between the nuclear spins and the fluctuating magnetic moments in the electronic system. In the paramagnetic insulating state, the experimental rate is accounted for by $\tau_c \simeq \omega_{ex}^{-1}$, where ω_{ex} is the exchange frequency for the fluctuating localized moments. In the metallic state, the effect of e-e correlations in lengthening τ_c relative to that expected in simple metals is considered to account for the rapid and only slightly temperature-dependent relaxation found experimentally.

Proton spin-lattice relaxation times of polycrystalline (NMP)(TCNQ) were measured by observing the recovery of the free induction magnetization after saturating the system with one or more 90° rf pulses. The temperature dependence of the rate T_1^{-1} is given in Fig. 1. The principal features are the magnitude of the relaxation rate (~100 sec^{-1}) and that the rates in metallic and insulating regimes are comparable, with no discontinuity. The observed relaxation times are much shorter than those found in related molecular solids without charge transfer, such as neutral
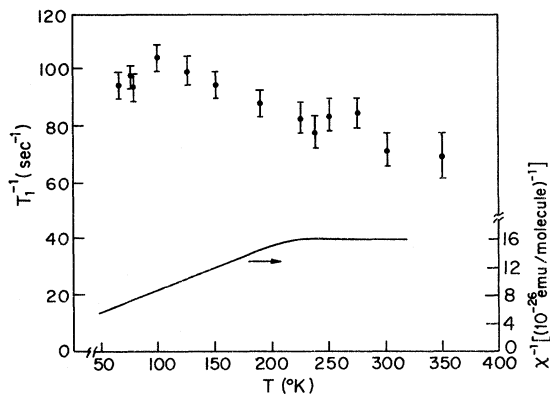

FIG. 1. Temperature dependence of T_1^{-1} for protons in (NMP)(TCNQ). The inverse static susceptibility is shown for comparison (Ref. 3).

TCNQ ($T_1 > 5$ min at 300°K). This, together with all the other solid-state properties of (NMP)-(TCNQ), indicates that the protons are strongly coupled to the electronic spin density (via the hyperfine interaction) and the measured relaxation times reflect the electronic state of the solid.[4]

In the paramagnetic insulating state ($30 \leqslant T \leqslant 200$°K), where susceptibility results[3] imply weakly coupled localized moments, the fluctuations in local field due to exchange give[5,6]

$$T_1^{-1} = \tfrac{1}{3}\sqrt{2\pi}(A/\hbar)^2 s(s+1)\omega_{ex}^{-1}, \qquad (1)$$

where A is the electron-nucleus interaction between spins s and I, respectively, and $\omega_{ex}^2 = (J/\hbar)^2 z s(s+1)$; J is the exchange coupling and z the number of nearest neighbors. There is no direct measurement of A in solid (NMP)(TCNQ); however, ESR hyperfine splittings for TCNQ$^-$ in solution give $A/g\mu_B = 1.57$ G.[7] It is reasonable to use this value for (NMP)(TCNQ) since the molecular wave function, and hence the spin density in the TCNQ$^-$ ion, is expected to be unchanged in the solid as compared with the ion in solution. This is equivalent to a tight-binding approximation which is valid for this system because the bandwidth (0.1 eV) is much less than the intramolecular level splittings (~2 eV) of TCNQ$^-$. An estimate of the dipolar field leads to a contribution to T_1^{-1} less than 10% of that from the hyperfine interactions. The exchange coupling [based on $H = 2J\sum \vec{s}_i \cdot \vec{s}_j$ as used in obtaining Eq. (1)][5] is $J = 2.6 \times 10^{-3}$ eV.[3] Using these values with $z = 2$ and $s = \tfrac{1}{2}$, Eq. (1) predicts $T_1^{-1} = 90$ sec^{-1}. Thus, the predicted rate fully accounts for the experimentally measured T_1. In the intermediate coupling regime appropriate to (NMP)(TCNQ) the concept of well-formed localized moments in the insulating phase is itself only approximately valid as discussed in Ref. 3. Nevertheless, the agreement must be considered satisfactory.

The role of the e-e interaction in the enhancement of the nuclear spin-lattice relaxation in metals was first treated quantitatively by Moriya.[8] He demonstrated that for a conduction-electron-nucleus interaction of the form $A(r)\vec{s} \cdot \vec{I}$, the relaxation rate can be written as

$$T_1^{-1} = (k_B T/2\mu_B \hbar^2)\sum_q |A_q|^2 \chi''(q, \omega_0)/\omega_0, \qquad (2)$$

where $A_q = \langle k + q | A(r) | k \rangle$ is the matrix element between two Bloch states (assumed to be k independent),[9] and $\chi''(q, \omega_0)$ is the imaginary part of the electronic susceptibility with wave vector q at the NMR frequency ω_0. Thus the e-e interaction effect on T_1^{-1} is the same as that for χ''. In the

independent particle approximation,

$$\chi_0(q, \omega) = \tfrac{1}{2} g^2 \mu_B{}^2 \sum_k \frac{n_k - n_{k+q}}{\epsilon_{k+q} - \epsilon_k - \hbar\omega + i\eta}, \qquad (3)$$

where n_k and ϵ_k are the respective number operators and energies for momentum k and $\eta = +0$. In one dimension at $T = 0°K$, the real part diverges at $q = 2k_F$. At finite temperatures, $\chi_0'(q, \omega)$ must be evaluated numerically. Examples of $\chi_0'(q, \omega)$ for several temperatures are given in Fig. 2 for a tight-binding band structure $\epsilon_k = 2t(1 - \cos ka)$ ($E_F = 2t$; $k_F = \pi/2a$, where a is the lattice constant). The imaginary part χ_0'' can be written, for $\hbar\omega \ll E_F$, as

$$\chi_0''(q, \omega) \cong \tfrac{1}{2} g^2 \mu_B{}^2 \hbar\omega \eta(\epsilon_{k_0}) \frac{\partial f}{\partial \epsilon}\bigg|_{\epsilon = \epsilon_{k_0}}, \qquad (4)$$

where k_0 is the solution of the equation $|\epsilon_{k_0} - \epsilon_{k_0 + q}| = \hbar\omega$, which in one dimension is a function of $|q|$ only; $\eta(\epsilon)$ is the density of states; and $f(\epsilon)$ is the Fermi function. At low temperatures ($k_B T \ll E_F$), $\partial f/\partial \epsilon \sim \delta(\epsilon - E_F)$, and since the only finite wave vector connecting two points on the Fermi surface (in the relevant direction) is q
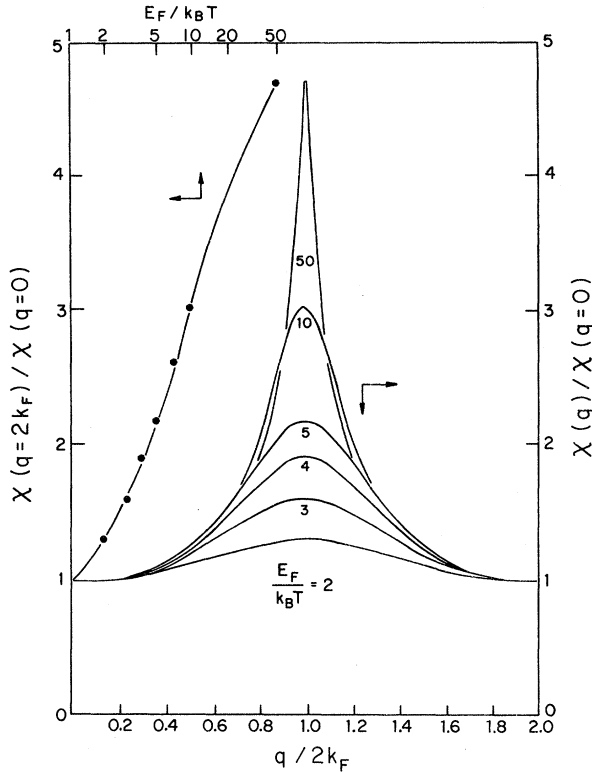

FIG. 2. The Lindhard function for a half-filled 1D tight-binding band for various ratios of $\beta = E_F/k_B T$. The peak value is shown in the upper left corner as a function of β.

$= 2k_F$, $\chi''(q, \omega)$ has appreciable values only for $q \approx 2k_F$. Thus by measuring the nuclear relaxation in a 1D metal at temperatures less than the Fermi temperature, one measures directly $\chi''(q \simeq 2k_F, \omega_0)$. Within the RPA and in the limit $\hbar\omega \ll E_F$,

$$\chi''(q, \omega) = \chi_0''(q, \omega)[1 - U_C(q)\chi_0'(q, \omega)]^{-2}. \qquad (5)$$

Hence, $T_1{}^{-1} = (T_{1,0})^{-1}\overline{K}$, where $(T_{1,0})^{-1}$ is the relaxation rate in the absence of the e-e interaction and $\overline{K}$ is defined by

$$\overline{K} = \frac{\int_{B.Z.} |A_q|^2 \chi_0''(q, \omega_0) \, dq [1 - U_C(q)\chi_0'(q)]^{-2}}{\int_{B.Z.} |A_q|^2 \chi_0''(q, \omega_0) \, dq}, \qquad (6)$$

which for $T \ll T_F = E_F/k_B$ has the value $\overline{K} = [1 - U_C(2k_F)\chi_0'(2k_F)]^{-2}$. Neglecting initially the enhancement effects, well above the metal-insulator (M-I) transition, one might expect the relaxation rate to be given by $T_{1,0}{}^{-1}$, the Korringa rate for a noninteracting metal,[6]

$$T_{1,0}{}^{-1} = (\pi/\hbar \mu_B{}^2)(A/g\mu_B)^2 \chi_P{}^2 k_B T, \qquad (7)$$

where $\chi_P = \mu_B{}^2/\pi t$ is the Pauli susceptibility for the 1D half-filled band. The measured spin susceptibility for (NMP)(TCNQ) is indeed temperature independent in the metallic regime and has the value $\chi_{meas} = 6.2 \times 10^{-28}$ emu/molecule (3.7×10^{-4} emu/mole).[3] Assuming that the exchange enhancement is of order 1, one would estimate for the Korringa rate $(T_{1,0}T)^{-1} \approx 4 \times 10^{-3}$ (sec °K)$^{-1}$, which is about 2 orders of magnitude smaller than the rate found experimentally. Thus, the unenhanced Korringa relaxation cannot account for the order of magnitude of the relaxation in the metallic state; the e-e interaction enhancement effect discussed above is extremely important. We emphasize again that both susceptibility data and transport properties indicate a metallic state above 200°K. The analysis of the T_1 data on the basis of a (possibly enhanced) Korringa mechanism is thus implied. Moreover, proton relaxation measurements in another compound of this family, (quinolinium)(TCNQ)$_2$, where correlation effects are less severe, show that in the metallic state $T_1{}^{-1}$ is proportional to the temperature over a wide range (100–300°K),[10] as would be predicted by the Korringa mechanism.

The problem is equivalent to the calculation of the electronic susceptibility in the metallic state near the M-I transition, taking into account both the e-e interaction and the band structure. As a first approximation we use the RPA result given in Eq. (5). This approximation for calculating T_1

has been used successfully in the 3D cases of alkali and noble metals (where, however, the effects are small).[11] In our 1D case near the M-I transition, the validity of the RPA is questionable. However, it should provide insight into what happens near the M-I transition and should give reasonable quantitative results at temperatures well into the metallic regime. To evaluate the enhancement we assume a tight-binding conduction band and complete screening of the e-e interaction, $U_C(q) = U_C$, i.e., the 1D Hubbard model. With these assumptions, $\bar{K}$, the enhancement factor, depends only on $\alpha = U_C \eta(E_F)$ and on the transfer integral t. The resulting equations are

$$K(\alpha, \beta) = \bar{K}(1 - \alpha)^2, \qquad (8)$$

$$\chi_{\text{meas}} = \chi_P(1 - \alpha)^{-1}, \qquad (9)$$

where $\bar{K}$ is given in Eq. (6), and $\alpha = U_C \eta(E_F)$. $K(\alpha, \beta)$ is the "Korringa enhancement factor" defined by

$$T_1^{-1} = (\pi/\hbar\mu_B^2)(A/g\mu_B)^2 \chi_{\text{meas}} k_B T K(\alpha, \beta).$$

The set of Eqs. (8) and (9) can be solved numerically. Using the highest temperature in deference to RPA ($T_1^{-1} = 75$ sec^{-1} at 300°K), one finds $K(\alpha, E_F, 300°K) \simeq 60$. This result, together with $\chi_{\text{meas}} = 6.2 \times 10^{-28}$ emu/molecule,[3] gives $t = 5 \times 10^{-2}$ eV and $\alpha = 0.45$. This value for t is of the same magnitude but approximately twice that found from analysis of the low-temperature data ($t = 2 \times 10^{-2}$ eV).[3] The apparent change in t suggests that the transition from insulator to metal is accompanied by a change in effective bandwidth as a result of the change in the many-electron wave function of the system. The larger value of $t = 0.05$ eV in the metallic state agrees with that obtained from a simple analysis of the metallic thermoelectric power.[3] Moreover, since the Fermi temperature, $k_B T_F = 2t$, is about 1150°K, a truly temperature-independent Pauli susceptibility is to be expected in the metallic regime ($T/T_F < 0.25$), in agreement with experiment.[3]

We note that in $\alpha = U_C \eta(E_F)$ which appears in the generalized RPA, the effective interaction U_C is not expected to be the bare interaction measured in the insulating state, but should be reduced due to the Fermi-liquid Coulomb-hole correlation.[3] Kanamori[12] derived an expression for U_C which, for 1D tight-binding band structure, can be written

$$U_C = U[1 + U/4\pi t]^{-1}. \qquad (10)$$

Although strictly valid only in the low-density limit, Eq. (10) can be expected to give a semi-quantitative estimate. Using Eq. (10) and the value $t = 0.05$ eV appropriate to the metallic state, $\alpha = 2U/(U + 4\pi t) = 0.45$ from which we obtain the bare interaction, $U = 0.18$ eV. The result is in precise agreement with that obtained directly from the low-temperature data.

Measurements of the nuclear relaxation thus provide information on the electronic correlation time in the vicinity of the M-I transition. In the paramagnetic state well below the transition, τ_c is deduced from the theory of fluctuating magnetic moments, whereas in the metallic state well above the transition the correlation time is deduced using the theories of electron-electron effects in enhancing the susceptibility. Surely the simple RPA result breaks down near the M-I transition where there is as yet no available theory for calculating τ_c. We have shown, however, that in the metal the generalized RPA yields reasonable results for t and $\alpha = U_C \eta(E_F)$. Moreover, extending the RPA to lower temperatures predicts the experimentally observed constant static susceptibility, whereas $\chi'(q = 2k_F)$ is found to diverge at $T \simeq 200°K$. Although this divergence will undoubtedly be suppressed in a better theory, the critical temperature is in good agreement with the observed M-I boundary. We conclude that e-e interaction effects play a dominant role in the metallic state of this 1D metal.

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Observation of a Time-Dependent Recoilless Fraction*†

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We have directly observed a time-dependent recoilless fraction. This effect is seen using delayed-coincidence Mössbauer spectroscopy. The time-dependent recoilless fraction is observed at the Fe^{3+} site and not at the Fe^{2+} site in a $CoSO_4 \cdot 7H_2O$ source. The relaxation time of the recoilless fraction is estimated to be between 10 and 100 nsec. Delayed-coincidence Mössbauer spectroscopy measurements on sources of $CoCl_2 \cdot 6H_2O$ and $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$ did not show such an effect.

Several authors[1-5] have pointed out the possibility of observing an excited localized mode of vibration using the Mössbauer effect. The general idea is that a relatively energetic nuclear event preceding the Mössbauer transition sets the nucleus vibrating with respect to its equilibrium position in the lattice. This vibrational state will exhibit a mean square nuclear displacement which is not, in general, equal to the thermal-equilibrium value. This "heated localized mode" will eventually relax. The relaxation rate will depend on the rate at which the localized-mode's energy can be transferred into the normal modes. The recoilless fraction depends on the mean square displacement of the radiating nucleus. Therefore, if the lifetime of this vibrational mode is of the same order as the lifetime of the nuclear state, the resulting Mössbauer energy spectrum will reflect the modulation of the exponential decay by this recoilless-fraction relaxation. Thus the spectrum will differ from the one obtained if the vibrational mode decayed very quickly. In the simplest cases, the existence of a time-dependent recoilless fraction would produce a reduction in the Mössbauer effect and in particular a narrowing of the Mössbauer peaks. These effects are not easy to see unambiguously using the regular Mössbauer effect. Indeed, the linewidth and intensity obtained in the absence of a time-dependent recoilless fraction depend on

sample thickness, collimation geometry, and nuclear environmental inhomogeneities.

The technique of delayed-coincidence Mössbauer spectroscopy (DCMS) permits the experimentalist to look directly at time-dependent effects. For the case of the Fe^{57} nucleus, the method is as follows. Co^{57} undergoes electron capture to form the second excited state of the Fe^{57} nucleus which decays by the emission of a 122-keV γ ray to the 14.4-keV first excited state. The detection of the 122-keV γ ray signals the formation of the 14.4-keV Mössbauer level. By using this "signal" γ ray in delayed coincidence with the 14.4-keV γ ray, a transmission experiment can be performed corresponding to a preset time interval with respect to the "signal" γ ray; i.e., time $t = 0$. (See Hoy, Hamill, and Wintersteiner[6] for a more complete review of the technique.) The modification of the Mössbauer transmission line shape, due to time selection only, has been calculated classically[7] and quantum mechanically.[8] The results are called "time filtering" and have been experimentally checked quantitatively.[9]

Figure 1 shows the calculated results for a single-line Mössbauer spectrum according to time filtering. The preset time intervals have been chosen to agree with our experimental time windows. In this time-filtering calculation there is only one free parameter, which is the size of the dip. Once this parameter is set for one time