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Conversion of Spin Species in Solid CH₄ through Level Crossing with Paramagnetic Impurities

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Measurements of proton spin-lattice relaxation times T_1 in γ -irradiated CH₄ at 1.1°K have been used to observe spin conversion. A strong magnetic field dependence of the conversion rate is found, with a sharp peak at 12.5 kOe and with some indication of a second peak at 15.2 kOe. The existence of the two peaks is tentatively interpreted as corresponding to transitions from a slightly split T level ($J=0$) to the ground A level ($J=0$).

The methane molecule CH₄ is known to have three different spin symmetry species, A , T , and E , with total nuclear spins $I=2$, 1, and 0, respectively. The lowest allowed rotational levels for the free molecule are $J=0$, 1, and 2, respectively. In the solid, the spin symmetry species conserve their identity. Spin conversion due to depopulation of the upper rotational levels at low temperatures has been observed by several authors.¹⁻⁴ The experimental results are consistent with the energy-level scheme shown in Fig. 1. The lowest level is the ground rotational level $J=0$ with a fivefold spin degeneracy (A -type molecules). The only excited level populated at liquid-helium temperatures is the T level $J=1$, $I=1$. It is ninefold degenerate in a cubic field, but it may be split by a trigonal crystal field into a sixfold degenerate level at a distance ϵ_1 from the ground state and a triplet at ϵ_2 . The results published so far do not allow a precise determination of ϵ_1 and ϵ_2 . The heat-capacity measurements are difficult because of the long conversion times. On the other hand, an absolute measurement of the nuclear magnetic susceptibility is not very accurate, particularly since its value changes only by a factor of 2 over the whole temperature range.

In this Letter, we report a measurement of the splitting using a different approach. The conversion $T \rightarrow A$ is very slow in pure methane. The conversion rate is increased by the presence of paramagnetic impurities. This has been observed in CH₄ and O₂ impurities^{1,3,4} and is a result of the mixing of the T and A states by an inhomogeneous magnetic field set up by the magnetic dipole moment $\vec{\mu}$ of the impurity. Besides this static effect, an impurity with a magnetic moment $\vec{\mu} = g\mu_B \vec{S}$ can give rise to a resonant effect. An applied magnetic field has no influence on the molecular energy-level spacing, while giving rise to a Zeeman splitting of the impurity levels. If $\epsilon_i = g\mu_B \vec{S} \cdot \vec{H}$, a phononless energy transfer can take place between the CH₄ molecules and the

		degen.	J	I
T	ϵ_1	3	1	1
	ϵ_2	6		
A	0	5	0	2

FIG. 1. Energy levels of CH₄ at $T < 10^\circ\text{K}$.

paramagnetic impurity. If such magnetorotational flip-flops are efficient compared with the intrinsic conversion, the field dependence of the conversion rate gives direct information about splitting and width of the rotational energy levels.

The magnetic properties of O₂ in solid CH₄ are not known and, moreover, we have found that conversion rates in CH₄ containing O₂ are not reproducible. For these reasons, we have used free radicals, produced by γ irradiation of CH₄ at 4.2°K.⁵ The EPR spectrum shows four lines from CH₃ with a hyperfine splitting of ~25 G and two lines separated by ~500 G resulting from hydrogen atoms. The spectrum is centered on g=2. The ⁶⁰Co γ source had an intensity of 2.2 Mrad/h, and the integrated dose rate for our sample was 40 Mrad. This corresponds to a radical concentration of 0.13 mol%, if we use the radical yield given for CD₄.⁶ The sample used in our experiment contained 30 ppm of O₂, as measured from T₁, in the liquid.⁷

In order to determine the conversion rate, we have measured the proton spin-lattice relaxation time T₁ rather than the susceptibility. This is an indirect, but more sensitive method. In fact, the relaxation time at thermal equilibrium T₁[∞] changes from 160 msec at 4.2°K to 610 msec at 1.1°K. The reason is that T molecules relax quickly because of their intrinsic relaxation time T₁^T,⁸ while the A molecules can only relax via the T species. Both species are abundant in the temperature range investigated and their nuclear

resonance frequency is the same. We can, therefore, safely assume a single spin temperature for their Zeeman energies. Paramagnetic impurities turn out to contribute negligibly to the relaxation, since the same relaxation times are found as in pure methane⁸ with a T₁ minimum at 6°K and an increase towards higher temperatures. Molecular hydrogen produced by the irradiation does not influence our measurements either: The sample was kept in liquid helium for 10 weeks, sufficient to convert most of the ortho-H₂ into the para state, and no change in the sample properties was found. Under the above conditions, we can write the measured relaxation time in terms of the heat capacities C_T and C_A and the populations P_T and P_A of the two species,

$$(T_1)^{-1} = [C_T / (C_T + C_A)] (T_1^T)^{-1} = [2P_T / (2P_T + 6P_A)] (T_1^T)^{-1} \quad (1)$$

Since the dependence of T₁^T on P_T and P_A is not known, these quantities cannot be obtained from measurements of T₁ using Eq. (1).

The conversion rates v_c are obtained in the following way: The sample, initially at thermal equilibrium at 4.2°K (T₁ = 160 msec) is quickly cooled to 1.1°K and the evolution of T₁ towards its new equilibrium value (610 msec) is observed as a function of time. The conversion times involved are long enough to measure T₁ at constant frequency by returning periodically for a short time from the conversion field to the measuring field. The measurements have been done at 30 MHz by standard pulse techniques. The curve

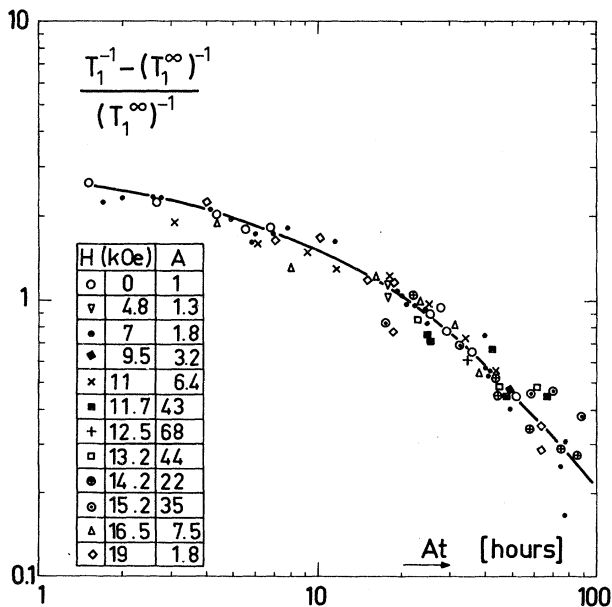


FIG. 2. Time dependence of T₁ at 1.1°K.

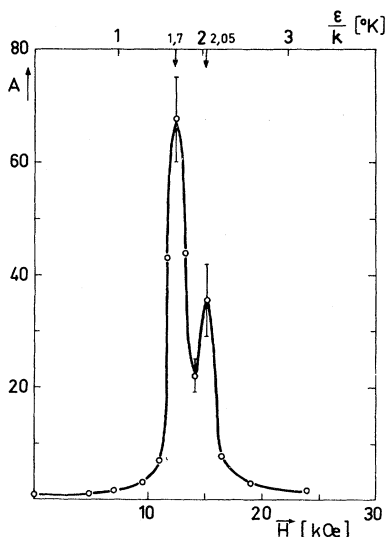


FIG. 3. Field dependence of the relative conversion rate at 1.1°K.

$(T_1)^{-1} - (T_1^\infty)^{-1} = f(t)$ 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 $T \rightarrow A$ 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 $q \approx 2k_F$ 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 $T = 0^\circ\text{K}$, 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 $\chi(q \approx 2k_F)$ 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 shown³ 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