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Multiexponential spin-lattice relaxation of ^{125}Te in tellurium due to ultraslow atomic motion

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Nonexponential spin-lattice relaxation is shown to result under selective excitation due to ultraslow site exchange. The hopping rate κ of the nuclei can be obtained directly without any further assumption on the nuclear spin interactions and spin thermodynamics. In tellurium single crystals, hopping rates of ^{125}Te less than $\kappa = 1$ sec^{-1} have been observed.

Slow and ultraslow atomic motion in solids has been investigated for a number of years now by NMR methods.[1] Particularly relaxation experiments in the "rotating frame" have been used extensively to study diffusion since the pioneering work of Redfield,[2] Slichter and Ailion,[3] and others. Abundant literature is available which deals with these techniques and their interpretation.[4]

In this Communication we want to propose a novel technique for the investigation of slow and ultraslow motion in solids which does not depend at all on the knowledge of the type or strength of nulcear spin interactions, i.e., the hopping rate κ of the nuclear spin can be extracted from the experiment directly without any further assumption. This leads to highly reliable and accurate results. Our technique will be applicable in all cases, where different nuclear sites result in different spectral lines, i.e., in all cases where high resolution NMR spectra in solids are observed.[5]

These may result from chemical shift or quadrupole interactions in noncubic single crystals or powder samples. The spectra should be resolved only in the sense that the linesplitting exceeds the homogeneous linewidth. No long-time rf irradiation which may cause excessive heating like in $T_{1\rho}$ experiments is necessary.

To be specific we want to treat the case of ^{125}Te diffusion in ultrapure tellurium single crystals. NMR spectra[6] and relaxation data of this system have been obtained before.[7,8] In Fig. 1 the three-line spectrum, resulting from the three different orientations of the chemical shift tensor in the unit cell is shown. For $\vec{B}_0$ parallel c, where c is the chain axis a single line spectrum is obtained. In an ordinary spin-lattice-relaxation experiment (T_1) all spectral lines are saturated or inverted by, e.g., a π pulse and their recovery with the relaxation time T_1 is observed. In the case of slow motion the relaxation rate $1/T_1$ can be exceedingly small. Let us suppose, that we irradiate selectively only, e.g., line 1 of the spectrum. There will be a "local" relaxation rate $1/T_1$ due to direct and indirect phonon processes as well as contributions from conduction electrons (in semiconductors and metals).[8] Moreover, at sufficiently large temperatures hopping of the nuclei via translational atomic diffusion occurs with a mean rate κ. The hopping process does reduce the magnetization $m_{Z1}(t)$ of the line 1 since magnetization is carried from line 1 to lines 2 and 3. Lines 2 and 3, however, do not supply magnetization to line 1 during hopping initially since their initial magnetization is considered to be zero.

For arbitrary initial condition the following set of coupled differential equations results

$$\frac{d}{dt}\vec{m}_Z(t) = -\underline{R}\cdot\vec{m}_Z(t) \quad , \tag{1}$$

with the formal solution

$$\vec{m}_Z(t) = \exp(-\underline{R}t)\vec{m}_Z(0) \quad , \tag{2}$$

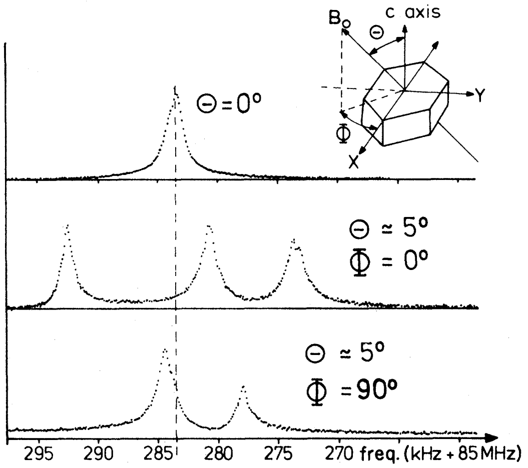

FIG. 1. NMR spectrum of ^{125}Te in a tellurium single crystal in a field $B_0 = 6.3$ T at room temperature.

where

$$\vec{m}_Z(t) = (m_{Z1}(t), m_{Z2}(t), m_{Z3}(t))$$

is a column vector and the relaxation matrix $\underline{R}$ can be expressed as

$$\underline{R} = \frac{1}{T_1}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \kappa \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} \quad . \tag{3}$$

The solution of Eq. (2) is in a straightforward manner obtained as

$$\exp(-\underline{R}t) = \exp\left(\frac{-t}{T_1}\right)\begin{pmatrix} a & b & b \\ b & a & b \\ b & b & a \end{pmatrix} \quad , \tag{4}$$

with

$$a = \tfrac{1}{3}(1 + 2e^{-3\kappa t}) \text{ and } b = \tfrac{1}{3}(1 - e^{-3\kappa t}) \quad . \tag{5}$$

Two limiting cases may be considered:

(i) All spectral lines are prepared in the same initial state, e.g., $m_{Z1}(0) = m_{Z2}(0) = m_{Z3}(0) = 1$ which leads to

$$m_{Zj}(t) = \exp(-t/T_1), \quad j = 1,2,3 \quad , \tag{6}$$

i.e., all lines relax with the same relaxation rate $1/T_1$.

(ii) Selective excitation of line 1, e.g.,

$$m_{Z1}(0) = 1, \quad m_{Z2}(0) = m_{Z3}(0) = 0 \quad ,$$

leads to nonexponential decay as

$$m_{Z1}(t) = \exp(-t/T_1)[1 + 2\exp(-3\kappa t)]/3 \quad , \tag{7a}$$

$$m_{Z2}(t) = m_{Z3}(t)$$

$$= \exp(-t/T_1)[1 - \exp(-3\kappa t)]/3 \quad . \tag{7b}$$

In the case of slow motion $(1/T_1 < \kappa << 1/T_2)$ this nonexponential relaxation behavior is most pronounced and the mean hopping rate κ can be determined directly from the measurements. Figure 2 shows this behavior for ^{125}Te in a tellurium single crystal for two different temperatures. The local background relaxation rate is caused mainly by charged vacancies as will be discussed in detail in a forthcoming paper. Furthermore, irradiation of all three lines, i.e., nonselective excitation leads to the usual exponential behavior as given by Eq. (6) with the background relaxation rate $1/T_1$ remaining unchanged. In contrast, the relaxation rate caused by the fluctuating chemical shift tensor with rate κ is extremely small; i.e., about 10^{-6} κ for a chemical shift anisotropy of about 1000 ppm.

It is straightforward to see that the rotating-frame magnetization $m_{Xj}(t)$ $(j = 1,2,3)$ in a spin-locking experiment, however, decays exponentially. Only spins *leaving* the spectral line j with a rate 2κ lead to a destruction whereas spins entering line j do not contribute since they appear with a random phase and cannot be locked in the locking field B_1. Starting from the same differential equation as before we arrive at

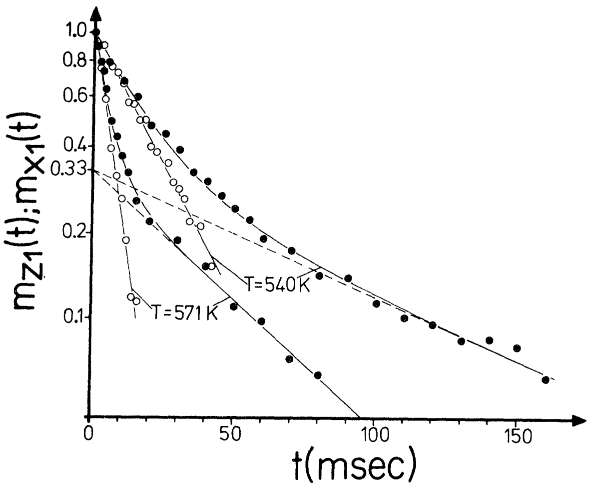

FIG. 2. Nonexponential time evolution of $m_{Z1}(t)$ (●●●) and $m_{X1}(t)$ (○○○) of a selectively excited line (1) of the ^{15}Te spectrum shown in Fig. 1 for two different temperatures. The data points compare extremely well with the theoretical expressions (lines) according to Eqs. (7a) and (10).

$$\vec{m}_X(t) = \exp(-\underline{R}_{1\rho}t)\vec{m}_X(0) \quad , \tag{8}$$

with

$$\underline{R}_{1\rho} = \left(\frac{1}{T_{1\rho}} + 2\kappa\right)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{9}$$

leading to an exponential decay

$$m_{Xj}(t) = m_{Xj}(0)\exp[-t(1/T_{1\rho} + 2\kappa)] \quad . \tag{10}$$

This behavior is demonstrated in Fig. 2, too.

Since $1/T_{1\rho}$ can be of the same order of magnitude as κ, $T_{1\rho}$ measurements seem to be more complicated in this situation. However, a differentiation can be obtained by varying the locking field B_1. Also spin echo (T_2) and linewidth measurements allow one to extract the hopping rate κ. Due to background contributions, however, these methods are by far less sensitive than the selective T_1 relaxation. An analysis of this sort will be presented elsewhere.

The cross-relaxation rates $1/T_{1\text{CR}} = 3\kappa$ and $1/T_{1\rho\text{CR}} = 2\kappa$ according to Eqs. (7a) and (10) were determined from selective relaxation measurements and are plotted versus temperature in Fig. 3. The data in Fig. 3 illustrate the proposed ratio $\frac{2}{3}$ of $1/T_{1\text{CR}}$ and $1/T_{1\rho\text{CR}}$.

Let us now compare the hopping rate κ obtained from our selective excitation with recent ^{127}Te^m tracer measurements performed in tellurium single crystals. Making use of a highly sophisticated sputtering technique, Mehrer *et al.*[9,10] were able to obtain tracer dif-

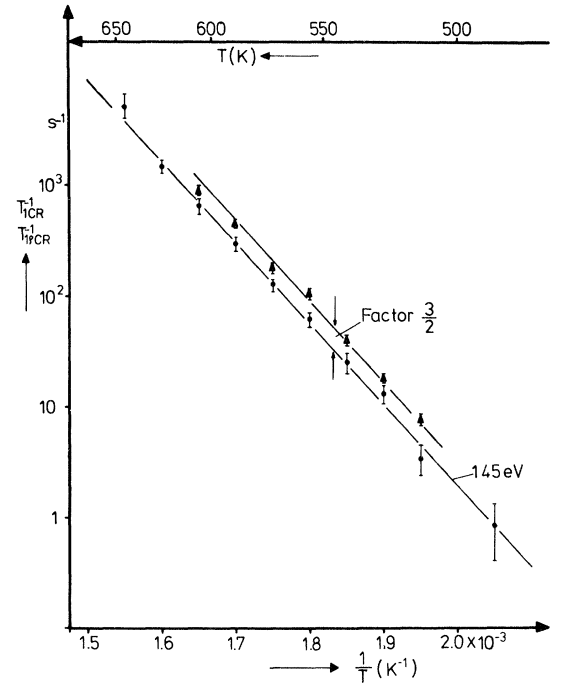

FIG. 3. Cross-relaxation rates $T_{1\mathrm{CR}}^{-1}=3\kappa$ (▲▲▲) and $T_{1\rho\mathrm{CR}}^{-1}=2\kappa$ (●●●) as defined in the text vs inverse temperature. An activation energy of 1.45 eV is determined from the slope. Note the theoretically expected $\frac{3}{2}$ ratio of the two cross-relaxation rates.

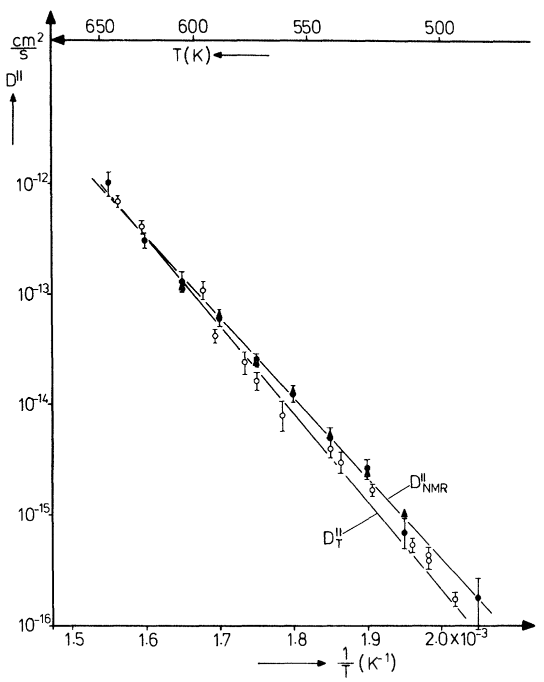

FIG. 4. Comparison of the diffusion coefficients $D^{\parallel}$ parallel to the c axis obtained from tracer measurements [$D_T^{\parallel}$ ○○○ Mehrer *et al.* (Refs. 9 and 10) and selective excitation relaxation [$D_{\mathrm{NMR}}^{\parallel}$ ●●● ($T_{1\rho\mathrm{CR}}$), ▲▲▲ ($T_{1\mathrm{CR}}$) this work].

fusion constants as low as 1.5×10^{-16} cm²/sec. Figure 4 shows their data for the tracer diffusion coefficient $D_T^{\parallel}$, i.e., parallel to the c axis of the crystal. Analogous to the expression for $D_T^{\parallel}$ of Mehrer *et al.*[9]

$$D_T^{\parallel}=(c/3)^2(\kappa_A+2\kappa_B)f_T^{\parallel}\ , \tag{11}$$

where c is the lattice constant along the c axis and $f_T^{\parallel}$ is the tracer correlation factor,[9] we define a NMR diffusion coefficient $D_{\mathrm{NMR}}^{\parallel}$ as

$$D_{\mathrm{NMR}}^{\parallel}=(c/3)^2\kappa=(c/3)^2\begin{cases}\frac{1}{3}1/T_{1\mathrm{CR}}\\ \frac{1}{2}1/T_{1\rho\mathrm{CR}}\ ,\end{cases} \tag{12}$$

where

$$\kappa=(\kappa_A+2\kappa_B)f_{\mathrm{NMR}}\ .$$

The NMR data are compared with the tracer data[9] in Fig. 4, demonstrating among others that $D_{\mathrm{NMR}}^{\parallel}$ can be determined down to 10^{-16} cm²/sec. Equation (11) is based on the assumption that atomic diffusion occurs via nearest-neighbor monovacancy jumps inside a tellurium chain (uncorrelated jump rate κ_A) and next-nearest-neighbor monovacancy jumps from one chain to another (uncorrelated jump rate κ_B). This leads to $\kappa=(\kappa_A+2\kappa_B)f_{\mathrm{NMR}}$ where the correlation factor f_{NMR} takes account of the temporal correlations in the atomic jump process (bunching effect[4]). The slight deviation of D_{NMR} and D_T evident from Fig. 4 is likely to be caused by the difference in the correlation factors and offers a possibility of determining the microscopic diffusion mechanism.[11]

We have demonstrated for the first time that selective excitation relaxation measurements open the possibility to investigate ultraslow motion directly without resorting to spin dynamics. In our case jump rates less than 1 sec⁻¹ were determined, however, this novel approach will stimulate investigations in other systems, e.g., ^{77}Se in selenium or ^{13}C in molecular crystals, where values below 10^{-2} sec⁻¹ will be observable due to the weak background relaxation.

Finally we would like to draw attention to related techniques in ESR[12] and recent[13] 2D NMR applied to site exchange.

ACKNOWLEDGMENTS

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[1] D. C. Ailion, in *Advances in Magnetic Resonance,* edited by J. S. Waugh (Academic, New York, 1971), Vol. 5, p 177.

[2] A. G. Redfield, Phys. Rev. 98, 1787 (1955).

[3] C. P. Slichter and D. G. Ailion, Phys. Rev. A 135, 1099 (1964).

[4] D. Wolf, *Spin-temperature and nuclear-spin relaxation in matter* (Clarendon, Oxford, 1979).

[5] M. Mehring, *High-resolution NMR spectroscopy in solids in NMR: Basic Principles and Progress* (Springer, Berlin, 1976), Vol. 11.

[6] M. Bensoussan, J. Phys. Chem. Solids 28, 1533 (1967).

[7] A. Koma, A. Hojo, and S. Tanaka, Phys. Lett. 28A, 95 (1968).

[8] H. Selbach, O. Kanert, and D. Wolf, Phys. Rev. B 19, 4435 (1979).

[9] H. Mehrer, M. Werner, and H. Siethoff, in Proceedings of the March meeting of the DPG, Münster, Germany, 1981 (unpublished), p. 364.

[10] H. Mehrer, M. Werner, and H. Siethoff (unpublished).

[11] G. Brünger, O. Kanert, and D. Wolf, Phys. Rev. B 22, 4727 (1980).

[12] J. S. Hyde and L. R. Dalton, Chem. Phys. Lett. 16, 568 (1972).

[13] J. Jeener, B. H. Meier, P. Bachmann, and R. R. Ernst, J. Chem. Phys. 71, 4546 (1979).