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Nuclear-magnetic-resonance methods for identifying and studying diffusion of different spin species in heteronuclear systems

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We introduce a new dipolar relaxation time T_{1D}' which characterizes the spin-lattice relaxation of secular dipolar interactions in the presence of a large rf field. Measurements of T_{1D}' are particularly useful for studying slow atomic motions in multispin systems, since such measurements enable us to vary the contribution of a particular spin species's motion relative to the contribution of the other spin species's, thus enabling us to identify the diffusing species. We also show that the anisotropy of the conventional dipolar relaxation time T_{1D} can differ enormously for diffusion of different spin species in a multispin system and, accordingly, can be used to identify the dominant diffusing species. Finally, we show that the high-rf-field rotating-frame relaxation time $T_{1\rho}$, measured as a function of rf frequency, also enables us to identify the diffusing species. We demonstrated experimentally the validity of these techniques by measurements of potassium vacancy diffusion in a KF:Ca^{++} single crystal and measurements of fluorine diffusion in AgF powder.

I. INTRODUCTION

NMR is currently widely used for studying the microscopic behavior of systems containing diffusing atoms and rotating molecules. Measurements of the temperature dependence of the spin-lattice relaxation time T_1 allow the determination of activation energies and jump times.[1,2] Similar measurements of the rotating-frame spin-lattice relaxation time $T_{1\rho}$ and of the dipolar relaxation time T_{1D} enable one to obtain information characteristic of much slower motions occuring at lower temperatures.[3-7] Both the T_1 theories[8,9] and more recently the high-rf-field $T_{1\rho}$ theories[10,11] have been extended to heterogeneous (multispin) systems.

A difficulty arises if one measures relaxation times in a multispin system. Such measurements by themselves will not normally indicate which spin species is diffusing, since a diffusion jump of any spin species may contribute to the relaxation. To obtain information about *which* species in diffusing, it is necessary to find some experimentally controlled parameter whose variation changes the contribution of one spin species's motion relative to the contribution of the others'. In this paper we present some examples of these parameters along with experimental verification of our ability to identify the diffusing species.

Consider the dipolar relaxation time T_{1D} for a multispin system. The different dipolar interaction terms normally cross relax rapidly to a common temperature, resulting in identical T_{1D} measurements for the different spin species.[12-19] In this paper we have extended the normal strong-collision Slichter-Ailion[3-6] (SA) theory for the dipolar relaxation time T_{1D} to the case of a two-spin (I and S) system. We then show that, for the case of strong I and weak S spins, there can be enormous anisotropy for diffusion of S spins, in contrast to the small anisotropy characteristic of the diffusion of I spins.[20,21] Thus the crystal orientation is an example of an easily controlled parameter whose variation can identify the diffusing species in a single crystal.

A major portion of this paper is devoted to describing a novel technique[22,23] for determining the dominantly diffusing species in a "slow motion" dipolar-relaxation-time experiment. In particular, we introduce a new relaxation time T_{1D}' which describes the spin-lattice relaxation of the secular part of the dipolar interaction in the presence of a large rf field. Furthermore, we develop an SA-type theory for relating T_{1D}' to the diffusion jump time. Like T_{1D} of the SA theory, T_{1D}' is appropriate for studying slow atomic motions but has a unique feature particularly suitable for multispin systems. By varying the orientation of the effective field in the rotating frame, the contribution to T_{1D}' of one spin species's motion may be varied relative to the others'. Thus, the dominantly diffusing spin species can easily be identified.

A third method for identifying the diffusing species consists of measuring the dependence of the high-field $T_{1\rho}$ on the orientation θ_I of the effective field in the rotating frame. We have derived expressions for $T_{1\rho}$ for a two-spin system (strong I and weak S) and have shown that the dependence of $T_{1\rho}$ on θ_I also depends strongly on which species is diffusing.

II. THEORY

A. Spins in a large dc field

Consider a system of two species of nuclear spins (I and S) in a solid. With the spin system placed in large dc magnetic field $\vec{H}_0$ (chosen to be along the z axis), the Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}_{ZI} + \mathcal{H}_{ZS} + \mathcal{H}_D \ . \tag{1}$$

The terms $\mathcal{H}_{ZI}$ and $\mathcal{H}_{ZS}$ are the Zeeman interactions of $\vec{H}_0$ with the I and S spins, respectively,

$$\mathcal{H}_{ZI} = -\hbar\gamma_I H_0 \sum_k I_{zk} \tag{2}$$

and

$$\mathcal{H}_{ZS} = -\hbar\gamma_S H_0 \sum_k S_{zk} \ . \tag{3}$$

The term $\mathcal{H}_D$ is the spin-spin dipolar interaction. It is divided into two parts, $\mathcal{H}_D^{(0)}$ and $\mathcal{H}_D^{(n)}$, the secular and nonsecular dipolar interactions, respectively,

$$\mathcal{H}_D = \mathcal{H}_D^{(0)} + \mathcal{H}_D^{(n)} \ . \tag{4}$$

The secular dipolar interaction is defined to be that part which commutes with $\mathcal{H}_{ZI}$ and $\mathcal{H}_{ZS}$ and is given by[8,24,25]

$$\mathcal{H}_D^{(0)} = \mathcal{H}_{DII}^{(0)} + \mathcal{H}_{DIS}^{(0)} + \mathcal{H}_{DSS}^{(0)} \ , \tag{5}$$

where

$$\mathcal{H}_{DII}^{(0)} = \frac{1}{2} \sum_{j,k} A_{jk}(3I_{zj}I_{zk} - \vec{I}_j \cdot \vec{I}_k) \ , \tag{6}$$

$$\mathcal{H}_{DIS}^{(0)} = \sum_{j,k} B_{jk} I_{zj} S_{zk} \ , \tag{7}$$

and

$$\mathcal{H}_{DSS}^{(0)} = \frac{1}{2} \sum_{j,k} C_{jk}(3S_{zj}S_{zk} - \vec{S}_j \cdot \vec{S}_k) \ . \tag{8}$$

The dipolar coupling constants, A_{jk}, B_{jk}, and C_{jk}, are given by

$$A_{jk} = \tfrac{1}{2}\gamma_I^2 \hbar^2 r_{jk}^{-3}(1 - 3\cos^2\theta_{jk}) \ , \tag{9}$$

$$B_{jk} = \gamma_I \gamma_S \hbar^2 r_{jk}^{-3}(1 - 3\cos^2\theta_{jk}) \ , \tag{10}$$

and

$$C_{jk} = \tfrac{1}{2}\gamma_S^2 \hbar^2 r_{jk}^{-3}(1 - 3\cos^2\theta_{jk}) \ . \tag{11}$$

We now write the Hamiltonian in the following form:

$$\mathcal{H} = \mathcal{H}_{ZI} + \mathcal{H}_{ZS} + \mathcal{H}_D^{(0)} + \mathcal{H}_D^{(n)} \ . \tag{12}$$

In a previous paper,[13] we showed that for large $\vec{H}_0$ the terms, $\mathcal{H}_{ZI}$, $\mathcal{H}_{ZS}$, $\mathcal{H}_D^{(0)}$, are quasi-invariants of the motion, each forming an energy reservoir whose spin order can be parametrized by a spin temperature. Thus, the density operator is written,[13,14,25,26] in the high-temperature limit,

$$\sigma = 1 - \beta_I \mathcal{H}_{ZI} - \beta_S \mathcal{H}_{ZS} - \beta_D \mathcal{H}_D^{(0)} \ , \tag{13}$$

where $\beta_I, \beta_S, \beta_D$ are inverse spin temperatures defined by

$$\beta = 1/kT \ . \tag{14}$$

Spin-lattice interactions cause the order of the energy reservoirs of $\mathcal{H}_{ZI}$, $\mathcal{H}_{ZS}$, and $\mathcal{H}_D^{(0)}$ to relax towards thermal equilibrium with the lattice. In other words, β_I, β_S, and β_D evolve with time towards the lattice temperature β_L. The time constants of this relaxation are defined to be T_{1I}, T_{1S}, and T_{1D} for the $\mathcal{H}_{ZI}$, $\mathcal{H}_{ZS}$, and $\mathcal{H}_D^{(0)}$ reservoirs, respectively (see Fig. 1).

Note that $\mathcal{H}_D^{(0)}$ includes *all* secular dipolar interactions, those between unlike spins as well as those between like spins [see Eq. (5)]. They all form a common reservoir with a common spin temperature. Thus, one cannot speak of "dipolar order" of the I spins separate from "dipolar order" of the S spins. Also, the relaxation time T_{1D} of dipolar order is the same for both I and S spins, as illustrated in Fig. 1. A variety of experiments[13-19,22] have been performed which demonstrate the validity of the single dipolar reservoir concept.

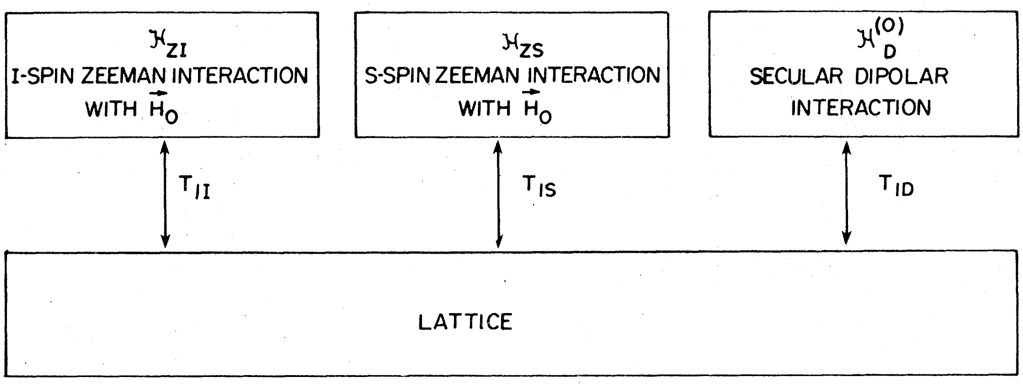

FIG. 1. Spin-lattice interactions with I and S spins in a large $\vec{H}_0$ in the lab frame.

B. Spins in a rotating reference frame

Consider the addition of a large rf field $\vec{\mathrm{H}}_{1I}$ (perpendicular to $\vec{\mathrm{H}}_0$) of frequency ω_I near the I-spin resonant frequency $\gamma_I H_0$. In a reference frame[27] rotating with frequency ω_I about $\vec{\mathrm{H}}_0$ (the z axis), the Hamiltonian of Eq. (1) becomes

$$\mathcal{H} = \mathcal{H}_{ZI}^{(r)} + \mathcal{H}_{ZS} + \mathcal{H}_D^{(0)} + \mathcal{H}_D^{(n)(r)} \quad . \tag{15}$$

Note that this transformation is made only with respect to the I spins and is accomplished by the unitary operator $\exp(-i\omega_I t \sum_k I_{zk})$. Thus the terms $\mathcal{H}_{ZS}$ and $\mathcal{H}_D^{(0)}$ remain unchanged since they commute with this operator.

The first term $\mathcal{H}_{ZI}^{(r)}$ in Eq. (15) is the Zeeman interaction of the I spins with an "effective" field $\vec{\mathrm{H}}_{\mathrm{eff}\,I}$ which[24,25] is the sum of $\vec{\mathrm{H}}_{1I}$ (which is now static in this reference frame) and an off-resonance field $\vec{\mathrm{h}}$, given by

$$\vec{\mathrm{h}} = \vec{\mathrm{H}}_0 - (\omega_I/\gamma_I)\hat{H}_0 \quad . \tag{16}$$

Thus the magnitude of $\vec{\mathrm{H}}_{\mathrm{eff}\,I}$ is

$$H_{\mathrm{eff}\,I} = (H_{1I}^2 + h^2)^{1/2} \quad , \tag{17}$$

and the angle between $\vec{\mathrm{H}}_{\mathrm{eff}\,I}$ and $\vec{\mathrm{H}}_0$ is given by

$$\theta_I = \tan^{-1}(H_{1I}/h) \quad . \tag{18}$$

If we tilt the z axis (with respect to the I-spins) by this angle θ_I such that it points along $\vec{\mathrm{H}}_{\mathrm{eff}\,I}$ (the "tilted rotating reference frame"[28]), the I-spin Zeeman interaction is written as

$$H_{ZI}^{(r)} = -\hbar\gamma_I H_{\mathrm{eff}\,I} \sum_k I_{zk} \quad . \tag{19}$$

The term $\mathcal{H}_D^{(n)(r)}$ in Eq. (15) is the nonsecular dipolar interaction $\mathcal{H}_D^{(n)}$ transformed to the rotating reference frame. Part of $\mathcal{H}_D^{(n)(r)}$ oscillates with frequencies ω_I and $2\omega_I$ in this reference frame and therefore can be neglected.[24] The time-independent part that remains is nonsecular with respect to $\mathcal{H}_{ZI}^{(r)}$ and $\mathcal{H}_{ZS}$.

We now divide the term $\mathcal{H}_D^{(0)}$ in Eq. (15) into two parts,[6,25,28,29] $\mathcal{H}_D^{(00)}$ and $\mathcal{H}_D^{(0n)}$, which are secular and nonsecular, respectively, with respect to $\mathcal{H}_{ZI}^{(r)}$. The secular part, which commutes with $\mathcal{H}_{ZI}^{(r)}$, is given (in the tilted rotating reference frame) by

$$\mathcal{H}_D^{(00)} = \mathcal{H}_{DII}^{(00)} + \mathcal{H}_{DIS}^{(00)} + \mathcal{H}_{DSS}^{(0)} \quad , \tag{20}$$

where

$$\mathcal{H}_{DII}^{(00)} = \tfrac{1}{2}[\tfrac{1}{2}(3\cos^2\theta_I - 1)] \times \sum_{j,k} A_{jk}(3I_{zj}I_{zk} - \vec{\mathrm{I}}_j \cdot \vec{\mathrm{I}}_k) \tag{21}$$

and

$$\mathcal{H}_{DIS}^{(00)} = \cos\theta_I \sum_{j,k} B_{jk} I_{zj} S_{zk} \quad . \tag{22}$$

The term $\mathcal{H}_{DSS}^{(0)}$ is given in Eq. (8).

Thus, we write the Hamiltonian as

$$\mathcal{H} = \mathcal{H}_{ZI}^{(r)} + \mathcal{H}_{ZS} + \mathcal{H}_D^{(00)} + (\mathcal{H}_D^{(0n)} + \mathcal{H}_D^{(n)(r)}) \quad . \tag{23}$$

This is similar in form to Eq. (12), that is, three commuting parts plus a noncommuting part. For large $\vec{\mathrm{H}}_{1I}$ the terms $\mathcal{H}_{ZI}^{(r)}$, ${}_{ZS}$, $\mathcal{H}_D^{(00)}$ are quasi-invariants of the motion, each forming an energy reservoir whose spin order can be parametrized by a spin temperature. The density operator is written as

$$\sigma = 1 - \beta_I^{(r)}\mathcal{H}_{ZI}^{(r)} - \beta_S\mathcal{H}_{ZS} - \beta_D^{(r)}\mathcal{H}_D^{(00)} \quad . \tag{24}$$

As before, spin-lattice interactions cause $\beta_I^{(r)}$, β_S, and $\beta_D^{(r)}$ to relax towards β_L. The time constants of this relaxation are defined to be $T_{1\rho I}$, T_{1S}, and T_{1D}' for the $\mathcal{H}_{ZI}^{(r)}$, $\mathcal{H}_{ZS}$, and $\mathcal{H}_D^{(00)}$ reservoirs, respectively (see Fig. 2). This definition of $T_{1\rho I}$ differs somewhat from that of Redfield[27] and that used in the strong-collision theory[3–6] as it characterizes only the relaxation of Zeeman order. However, in the large-field (large $\vec{\mathrm{H}}_{1I}$) case, the two definitions agree. The relax-

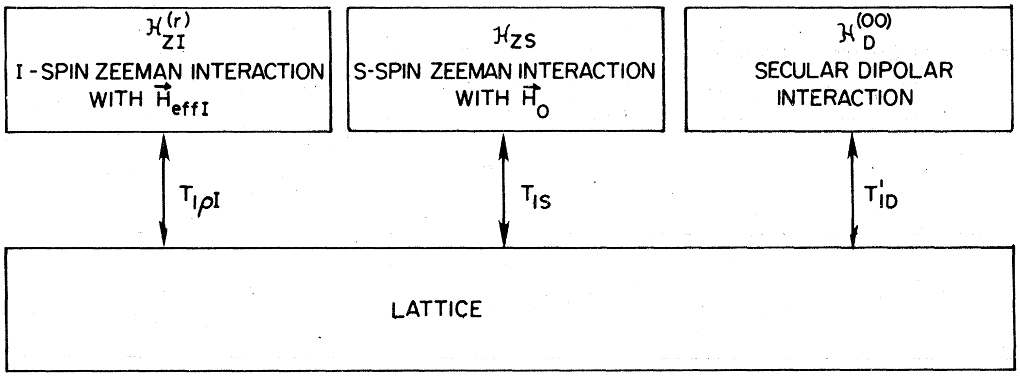

FIG. 2. Spin-lattice interactions with I and S spins in the rotating reference frame.

ation time T_{1D}' has only recently[12,22] been identified and defined and will be discussed in more detail in the following sections of this paper.

C. Strong-collision theory

Consider the case of dipolar spin-lattice relaxation due to slow atomic motion. By "slow", we mean that the average time interval τ between diffusion jumps of an atom is much greater than the spin-spin relaxation time T_2 (the time required for an energy reservoir to come to internal thermal equilibrium[25]). From the SA theory,[3-6] we obtain an expression for the dipolar relaxation time for this case:

$$\frac{1}{T_{1D}}=\frac{N}{\tau}\frac{\mathrm{Tr}(\mathcal{H}_{Di}^{(0)})^2-\mathrm{Tr}(\mathcal{H}_{Di}^{(0)}\mathcal{H}_{Df}^{(0)})}{\mathrm{Tr}(\mathcal{H}_{Di}^{(0)})^2}\quad, \tag{25}$$

where $\mathcal{H}_{Di}^{(0)}$ and $\mathcal{H}_{Df}^{(0)}$ are the secular dipolar Hamiltonians before and after a jump, respectively, and N is the number of jumping atoms in the spin system. [One should note that this equation differs from Eq. (1) of Ref. 22 by a minus sign. The right-hand side of Eqs. (1) and (5)–(7) of Ref. 22 should all be multiplied by minus one.] The last term in Eq. (25) represents the average fractional change of energy of the dipolar reservoir due to a single jump of an atom:

$$-\frac{\Delta E}{E}=\frac{\mathrm{Tr}(\mathcal{H}_{Di}^{(0)})^2-\mathrm{Tr}(\mathcal{H}_{Di}^{(0)}\mathcal{H}_{Df}^{(0)})}{\mathrm{Tr}(\mathcal{H}_{Di}^{(0)})^2}\quad. \tag{26}$$

In multispin systems, such as the present case, $\mathcal{H}_D^{(0)}$ includes *all* secular dipolar interactions, as seen in Eq. (5). Thus, the motion of any one of the spin species present affects T_{1D}. As an example, consider the case of diffusion in a system of strong I spins (γ_I large) and weak S spins (γ_S small). We then have

$$\mathcal{H}_{DII}^{(0)} >> \mathcal{H}_{DIS}^{(0)} >> \mathcal{H}_{DSS}^{(0)}\quad. \tag{27}$$

If T_{1D} is due to I-spin diffusion, we have from Eq. (25)

$$\frac{1}{T_{1D}}=\frac{1}{\tau_I}2(1-p_{II})\quad, \tag{28}$$

where $2(1-p_{II})$ is a geometric factor, of order 1, defined by

$$2(1-p_{II})=N_I\frac{\mathrm{Tr}(\mathcal{H}_{DIIi}^{(0)})^2-\mathrm{Tr}(\mathcal{H}_{DIIi}^{(0)}\mathcal{H}_{DIIf}^{(0)})}{\mathrm{Tr}(\mathcal{H}_{DIIi}^{(0)})^2}\quad. \tag{29}$$

The I-S and S-S interactions have been omitted because of their small size [see Eq. (27)]. Note that Eqs. (28) and (29) are the same as the SA result for the single-spin species case. This is because the S spins are weak and the relaxation of the dipolar reservoir, dominated by the I-I interactions, preceeds as if the S spins were not even present.

If, on the other hand, T_{1D} is due to S-spin diffusion, we have, from Eq. (25),

$$\frac{1}{T_{1D}}=\frac{1}{\tau_S}\frac{H_{LIS}^2}{H_{LII}^2+H_{LIS}^2}(1-p_{SI})\quad, \tag{30}$$

where $(1-p_{SI})$ is again a geometric factor, of order 1, defined by

$$1-p_{SI}=N_S\frac{\mathrm{Tr}(\mathcal{H}_{DISi}^{(0)})^2-\mathrm{Tr}(\mathcal{H}_{DISi}^{(0)}\mathcal{H}_{DISf}^{(0)})}{\mathrm{Tr}(\mathcal{H}_{DISi}^{(0)})^2}\quad. \tag{31}$$

The local fields, H_{LII} and H_{LIS}, are defined by

$$H_{LII}^2=H_0^2\frac{\mathrm{Tr}(\mathcal{H}_{DII}^{(0)})^2}{\mathrm{Tr}(\mathcal{H}_{ZI})^2} \tag{32}$$

and

$$H_{LIS}^2=H_0^2\frac{\mathrm{Tr}(\mathcal{H}_{DIS}^{(0)})^2}{\mathrm{Tr}(\mathcal{H}_{ZI})^2}\quad. \tag{33}$$

Note that in the numerator of Eq. (31), only I-S terms are present. This is due to the fact that $\mathcal{H}_{DIIi}^{(0)}$ and $\mathcal{H}_{DIIf}^{(0)}$ are equal in the case of S-spin diffusion. As before, S-S terms are omitted because they are negligibly small.

From Eqs. (27), (32), and (33), we see that $H_{LII} >> H_{LIS}$. Thus, from Eq. (30), we find that $T_{1D} >> \tau_S$ for S-spin diffusion. This is to be expected, since the weak S-spins' motion should surely have much less effect on the dipolar reservoir than would the strong I-spins' motion.

Another interesting feature of S-spin diffusion as contrasted to I-spin diffusion is the anisotropy in T_{1D} as predicted by Eq. (30). (Anisotropy refers to measurements as a function of sample orientation in $\vec{H}_0$ and enters the calculations through the value of θ_{jk} in the dipolar coupling parameters A_{jk}, B_{jk}, and C_{jk}.) The terms $2(1-p_{II})$ and $(1-p_{SI})$ usually have small anisotropy.[20,21] Thus, T_{1D} for I-spin diffusion [see Eq. (28)] would also have small anisotropy. On the other hand, T_{1D} anisotropy for S-spin diffusion [see Eq. (30)] is given approximately by the local-field term $H_{LIS}^2/(H_{LII}^2+H_{LIS}^2)$ which in some instances is very anisotropic. An example of large T_{1D} anisotropy in S-spin diffusion is given in the KF case, discussed in Sec. V.

D. Modified strong-collision theory for T_{1D}'

The SA theory is easily modified to give us an expression for T_{1D}' due to slow atomic motion. We simply change $\mathcal{H}_D^{(0)}$ to $\mathcal{H}_D^{(00)}$ and obtain

$$\frac{1}{T_{1D}'}=\frac{N}{\tau}\frac{\mathrm{Tr}(\mathcal{H}_{Di}^{(00)})^2-\mathrm{Tr}(\mathcal{H}_{Di}^{(00)}\mathcal{H}_{Df}^{(00)})}{\mathrm{Tr}(\mathcal{H}_{Di}^{(00)})^2}\quad. \tag{34}$$

Note that, since $\mathcal{H}_D^{(00)}$ is a function of θ_I [see Eqs. (20)–(22)], T_{1D}' is also. This is an important feature of T_{1D}'. It contains a parameter θ_I which is determined by an experimentally controlled variable ω_I, the frequency of $\vec{H}_{1I}$. Thus, by varying θ_I, the relative sensitivity of T_{1D}' to the motions of different spin species can be varied.

To illustrate this, consider the case treated in the previous section, that is, diffusion in a system of strong I spins and weak S spins. If T_{1D}' is due to I-spin diffusion, we have, from Eq. (34),

$$\frac{1}{T_{1D}'}=\frac{1}{\tau_I}\frac{[\frac{1}{2}(3\cos^2\theta_I-1)]^2H_{LII}^2}{[\frac{1}{2}(3\cos^2\theta_I-1)]^2H_{LII}^2+\cos^2\theta_I\,H_{LIS}^2}2(1-p_{II})+\frac{1}{\tau_I}\frac{\cos^2\theta_I\,H_{LIS}^2}{[\frac{1}{2}(3\cos^2\theta_I-1)]^2H_{LII}^2+\cos^2\theta_I\,H_{LIS}^2}(1-p_{IS})\;, \tag{35}$$

where $2(1-p_{II})$ is given by Eq. (29), and $(1-p_{IS})$ is a geometric factor of order 1, defined by

$$1-p_{IS}=N_I\frac{\mathrm{Tr}(\mathcal{H}_{DISi}^{(0)})^2-\mathrm{Tr}(\mathcal{H}_{DISi}^{(0)}\mathcal{H}_{DISf}^{(0)})}{\mathrm{Tr}(\mathcal{H}_{DISi}^{(0)})^2}\;. \tag{36}$$

The local fields, H_{LII} and H_{LIS}, are given by Eqs. (32) and (33). Note that in Eq. (35) the I-S interaction could not be neglected as it was in Eq. (28), since for θ_I near the magic angle $\theta_m(=\cos^{-1}\sqrt{1/3}\cong 54.7°)$ the I-I interaction [the first term in Eq. (35)] becomes very small so that the I-S interaction [the second term in Eq. (35)] may contribute significantly to T_{1D}'. For θ_I not near θ_m, the I-S interaction may be neglected, and Eq. (35) becomes

$$\frac{1}{T_{1D}'}=\frac{1}{\tau_I}2(1-p_{II})\;, \tag{37}$$

which is identical to T_{1D} given by Eq. (28). Thus, T_{1D}' in the case of I-spin diffusion is generally independent of θ_I, except perhaps near $\theta_I=\theta_m$. For $\theta_I=\theta_m$, the I-I interaction is zero, and Eq. (35) becomes

$$\frac{1}{T_{1D}'(\theta_m)}=\frac{1}{\tau_I}(1-p_{IS})\;. \tag{38}$$

By comparison of Eqs. (37) and (38), we see that the amount by which $T_{1D}'(\theta_I)$ varies near $\theta_I=\theta_m$ is determined by the relative values of $2(1-p_{II})$ and $(1-p_{IS})$.

In contrast, if T_{1D}' is due to S-spin diffusion, we have from Eq. (34)

$$\frac{1}{T_{1D}'}=\frac{1}{\tau_S}\frac{\cos^2\theta_I\,H_{LIS}^2}{[\frac{1}{2}(3\cos^2\theta_I-1)]^2H_{LII}^2+\cos^2\theta_I\,H_{LIS}^2}(1-p_{SI})+\frac{1}{\tau_S}\frac{H_{LSS}^2}{[\frac{1}{2}(3\cos^2\theta_I-1)]^2H_{LII}^2+\cos^2\theta_I\,H_{LIS}^2}2(1-p_{SS})\;, \tag{39}$$

where $(1-p_{SI})$ is given by Eq. (31), and $2(1-p_{SS})$ is a geometric factor, of order 1, defined by

$$2(1-p_{SS})=N_S\frac{\mathrm{Tr}(\mathcal{H}_{DSSi}^{(0)})^2-\mathrm{Tr}(\mathcal{H}_{DSSi}^{(0)}H_{DSSf}^{(0)})}{\mathrm{Tr}(\mathcal{H}_{DSSi}^{(0)})^2}\;. \tag{40}$$

The local field H_{LSS} is given by

$$H_{LSS}^2=H_0^2\,\mathrm{Tr}(\mathcal{H}_{DSS}^{(0)})^2/\mathrm{Tr}(\mathcal{H}_{ZI})^2\;. \tag{41}$$

Note that in Eq. (39) the S-S interaction cannot always be neglected as it was in Eq. (30), since, for θ_I near 90°, the I-S interaction [the first term in Eq. (39)] becomes very small so that the S-S interaction [the second term in Eq. (39)] may contribute significantly to T_{1D}'.

In the case of S-spin diffusion, T_{1D}' [see Eq. (39)] has a large dependence on θ_I. In particular, for $\theta_I=\theta_m$, Eq. (39) becomes

$$\frac{1}{T_{1D}'(\theta_m)}=\frac{1}{\tau_S}(1-p_{SI})\;. \tag{42}$$

Thus, $T_{1D}'(\theta_m)\sim\tau_S$ and is much smaller than T_{1D} given by Eq. (30). For $\theta_I=90°$, Eq. (39) becomes

$$\frac{1}{T_{1D}'(90°)}=\frac{1}{\tau_S}4\frac{H_{LSS}^2}{H_{LII}^2}2(1-p_{SS})\;. \tag{43}$$

In this instance, $T_{1D}'(90°) \gg \tau_S$ and in fact is also much larger than T_{1D} given by Eq. (30). Thus, $T_{1D}'(\theta_I)$ in the case of S-spin diffusion varies a large amount (often orders of magnitude) as a function of θ_I. This is an extremely important feature of T_{1D}'. By varying θ_I, we can vary the effect of S-spin diffusion on $T_{1D}'(\theta_I)$ relative to the effect of I-spin diffusion. This allows us to study the motions of different spins separately and identify them, as is illustrated in Sec. V.

E. High-field $T_{1\rho}$

Consider the rotating-frame Zeeman spin-lattice relaxation time $T_{1\rho I}$ due to atomic motion. (For large $\vec{H}_{1I}$, which is the present case, this relaxation time is often called the "high field" $T_{1\rho}$.) The expression for $T_{1\rho I}$ may be divided into two parts, $T_{1\rho II}$

and $T_{1\rho IS}$, due to contributions from the *I-I* and *I-S* dipolar interactions, respectively.

$$\frac{1}{T_{1\rho I}}=\frac{1}{T_{1\rho II}}+\frac{1}{T_{1\rho IS}} \quad . \tag{44}$$

An expression for $T_{1\rho II}$ was first given by Look and Lowe[7] for the case of $\vec{H}_{1I}$ on resonance and then later extended by Jones[30] to the off-resonance case. In the limit $\gamma_I H_0 \tau >> 1$ (corresponding to temperatures far below the T_1 minimum), Jones's expression reduces to

$$\frac{1}{T_{1\rho II}}=\tfrac{3}{8}\gamma_I^4 \hbar^2 I(I+1)$$
$$\times [\sin^2\theta_I \cos^2\theta_I \, J_{II}^{(0)}(\gamma_I H_{\text{eff}\,I})$$
$$+\sin^4\theta_I \, J_{II}^{(0)}(2\gamma_I H_{\text{eff}\,I})] \quad , \tag{45}$$

where $J_{II}^{(0)}(\omega)$ is the spectral density of the correlation function of the *I-I* secular dipolar interaction and depends on the nature of the atomic motion.

An expression for $T_{1\rho IS}$ has also been given[3k, 10, 32] for the case of $\vec{H}_{1I}$ on resonance ($\theta_I=90°$), which, in the limits $\gamma_I H_0 \tau >> 1$ and $\gamma_S H_0 \tau >> 1$, is written

$$1/T_{1\rho IS}(90°)=\tfrac{1}{6}\gamma_I^2\gamma_S^2\hbar^2 S(S+1)J_{IS}^{(0)}(\gamma_I H_{1I}) \quad , \tag{46}$$

where $J_{IS}^{(0)}(\omega)$ is the spectral density of the correlation function of the *I-S* secular dipolar interaction. As far as we have been able to determine, an extension of this expression for $T_{1\rho IS}$ to the off-resonance case has not yet been reported in the literature. It is, however, straightforward to provide one. Only two minor changes in Eq. (46) need be made. First, the *I*-spin Zeeman interaction $\mathcal{H}_{ZI}^{(r)}$ given by Eq. (19) involves $H_{\text{eff}\,I}$ instead of H_{1I}. This feature can be included in Eq. (46) by changing $J_{IS}^{(0)}(\gamma_I H_{1I})$ to $J_{IS}^{(0)}(\gamma_I H_{\text{eff}\,I})$. Second, the nonsecular dipolar interaction $\mathcal{H}_{DIS}^{(0n)}$ includes a factor $\sin\theta_I$. We obtain from Eqs. (7) and (22), in the tilted rotating reference frame,

$$\mathcal{H}_{DIS}^{(0n)}=-\sin\theta_I \sum_{j,k} B_{jk} I_{xj} S_{zk} \tag{47}$$

We can include this feature in Eq. (46) by changing B_{jk} to $\sin\theta_I B_{jk}$. Since Eq. (46) has a quadratic dependence on B_{jk} [note the $(\gamma_I\gamma_S)^2$ factor, for example, and compare with Eq. (10)], we simply multiply the expression by $\sin^2\theta_I$.

Finally, then, we have

$$\frac{1}{T_{1\rho IS}}=\tfrac{1}{6}\gamma_I^2\gamma_S^2\hbar^2 S(S+1)$$
$$\times \sin^2\theta_I J_{IS}^{(0)}(\gamma_I H_{\text{eff}\,I}) \tag{48}$$

In the limit $\gamma_I H_{\text{eff}\,I}\tau >> 1$ (corresponding to the cold side of the $T_{1\rho I}$ minimum), these expressions can be simplified. It is well known[9,33] that in this limit the spectral densities $J^{(0)}(\omega)$ are proportional to ω^{-2}. Thus,

$$J_{II}^{(0)}(2\gamma_I H_{\text{eff}\,I})=\frac{H_{1I}^2}{H_{\text{eff}\,I}^2}J_{II}^{(0)}(2\gamma_I H_{1I})$$
$$=\sin^2\theta_I J_{II}^{(0)}(2\gamma_I H_{1I}) \quad . \tag{49}$$

Using this and similar expressions, we obtain

$$\frac{1}{T_{1\rho II}}=\tfrac{3}{8}\gamma_I^4\hbar^2 I(I+1)J_{II}^{(0)}(2\gamma_I H_{1I})$$
$$\times \sin^4\theta_I(4\cos^2\theta_I+\sin^2\theta_I) \tag{50}$$

and

$$\frac{1}{T_{1\rho IS}}=\tfrac{1}{6}\gamma_I^2\gamma_S^2\hbar^2 S(S+1)$$
$$\times J_{IS}^{(0)}(\gamma_I H_{1I})\sin^4\theta_I \tag{51}$$

As an application of these expressions, consider the case treated in the previous sections, i.e., diffusion in a system of strong *I* spins and weak *S* spins. In the case of *I*-spin diffusion, $T_{1\rho I}$ is given by $T_{1\rho II}$ in Eq. (50). (The contribution from $T_{1\rho IS}$ is much too small to be significant at any value of θ_I.) Assuming a constant H_{1I}, then, we obtain from Eq. (50):

$$\frac{T_{1\rho I}(\theta_I)}{T_{1\rho I}(90°)}=\frac{1}{\sin^4\theta_I(4\cos^2\theta_I+\sin^2\theta_I)} \quad . \tag{52}$$

In the case of *S*-spin diffusion, $T_{1\rho II}$ does not contribute to $T_{1\rho I}$, and thus $T_{1\rho I}$ is given by $T_{1\rho IS}$ in Eq. (51). Assuming a constant H_{1I}, we have

$$\frac{T_{1\rho I}(\theta_I)}{T_{1\rho I}(90°)}=\frac{1}{\sin^4\theta_I} \quad . \tag{53}$$

A comparison of Eqs. (52) and (53) clearly shows that the θ_I dependence of $T_{1\rho I}$ is very much different in the two cases. Thus, by measuring $T_{1\rho}(\theta_I)$ as a function of θ_I (at constant H_{1I}), we can easily determine whether *I*-spin or *S*-spin diffusion dominates the relaxation.

III. EXPERIMENTAL METHODS

A. T_{1D}' pulse sequence

The pulse sequence for measuring T_{1D}' has been described briefly in a previous paper.[22] (Note that the first pulse sequence proposed for measuring T_{1D}' was a double-resonance sequence.[12] The pulse sequence described here is a single-resonance sequence. It is simpler and provides a larger signal than does the former.) Here we describe the T_{1D}' pulse sequence in more detail.

First we demagnetize the *I* spins (see Fig. 3) by

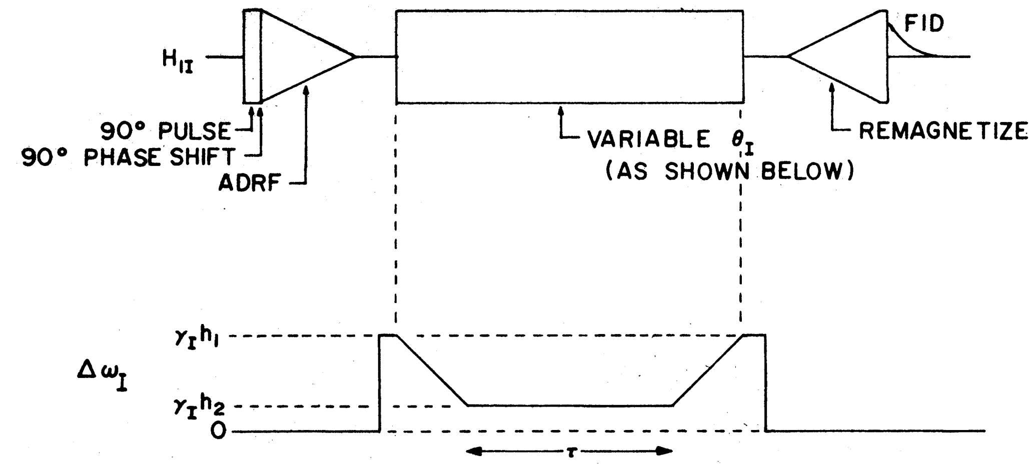

FIG. 3. Pulse sequence for measuring T_{1D}'. The lower figure shows the variation of $\Delta\omega_I = \gamma_I H_0 - \omega_I$, the off-resonance frequency of H_{1I}.

spin-locking[34] (i.e., a 90° pulse followed by a 90° phase shift) followed by adiabatic demagnetization in the rotating reference frame[35] (ADRF). This step transfers Zeeman order which was originally along $\vec{H}_0$ to dipolar order of the $\mathcal{H}_D^{(0)}$ reservoir.

We then apply $\vec{H}_{1I}$ at a frequency which is off resonance by an amount $\gamma_I h_1$. The dipolar reservoir is now properly described in the rotating reference frame, i.e., by $\mathcal{H}_D^{(00)}(\theta_{I1})$, where $\theta_{I1} = \tan^{-1}(H_{1I}/h_1)$. If we are sufficiently far off resonance ($\theta_{I1} \cong 0$), we see from comparison of Eqs. (20)–(22) with Eqs. (5)–(7) that $\mathcal{H}_D^{(00)}(\theta_{I1} \cong 0)$ is approximately equal to $\mathcal{H}_D^{(0)}$. Thus the dipolar order, which was in the $\mathcal{H}_D^{(0)}$ reservoir before $\vec{H}_{1I}$ was turned on, is preserved and is now in the $\mathcal{H}_D^{(00)}(\theta_{I1})$ reservoir.

We next sweep the frequency of $\vec{H}_{1I}$ to a value off resonance by an amount $\gamma_I h_2$. This process varies θ_I and accordingly varies $\mathcal{H}_D^{(00)}(\theta_I)$. If we sweep sufficiently slowly, the order of the $\mathcal{H}_D^{(00)}(\theta_I)$ reservoir is preserved at all times, and thus the process is adiabatic. The dipolar order is now in the $\mathcal{H}_D^{(00)}(\theta_{I2})$ reservoir, where $\theta_{I2} = \tan^{-1}(H_{1I}/h_2)$. Since $\mathcal{H}_D^{(00)}(\theta_I)$ varies as we sweep θ_I, the sweep process effectively sweeps the heat capacity of the dipolar reservoir.

The entire process has thus transferred Zeeman order originally along $\vec{H}_0$ to dipolar order of the $H_D^{(00)}(\theta_{I2})$ reservoir. Since the entire pulse sequence thus far has been adiabatic (i.e., spin order is preserved), the spin temperature can be calculated[25]:

$$\beta_D^{(r)} = \beta_L \left[\frac{\mathrm{Tr}(\mathcal{H}_{ZI})^2}{\mathrm{Tr}[\mathcal{H}_D^{(00)}(\theta_{I2})]^2} \right]^{1/2} . \tag{54}$$

Note that θ_{I2} is arbitrary and can be chosen to be any value desired. We hold the value of θ_I at θ_{I2} for a time τ, during which the dipolar order decays via spin-lattice relaxation. We write a rate equation for $\beta_D^{(r)}$ which defines T_{1D}':

$$\frac{d\beta_D^{(r)}}{dt} = -\frac{1}{T_{1D}'}(\beta_D^{(r)} - \beta_L) . \tag{55}$$

Since $\beta_D^{(r)} >> \beta_L$ initially [see Eq. (54)], $\beta_D^{(r)}$ decays essentially towards zero. Thus, from Eq. (55), we can write, to good approximation,

$$\beta_D^{(r)}(t) = \beta_D^{(r)}(0) \exp[-t/T_{1D}'(\theta_{I2})] . \tag{56}$$

After the time τ, we sweep the frequency of $\vec{H}_{1I}$ back off resonance (i.e., sweep θ_I back to θ_{I1}) and then turn $\vec{H}_{1I}$ off. This transfers any remaining dipolar order of $\mathcal{H}_D^{(00)}(\theta_{I2})$ back to dipolar order of $\mathcal{H}_D^{(0)}$. Remagnetization of the I spins further transfers this order to Zeeman order along $\vec{H}_{1I}$. The magnetization M_I, now along $\vec{H}_{1I}$, is less than the original M_{0I} by the factor $\exp[-t/T_{1D}'(\theta_{I2})]$ and is measured by turning off $\vec{H}_{1I}$ suddenly and then observing the free induction decay (FID). By repeating this pulse sequence for various values of τ, the spin-lattice relaxation time $T_{1D}'(\theta_{I2})$ can be determined using

$$M_I = M_{0I} \exp[-\tau/T_{1D}'(\theta_{I2})] . \tag{57}$$

We now examine in more detail some of the unique features of the T_{1D}' pulse sequence. To do so, it is useful first to develop a general expression for calculating the loss of spin order due to a sudden change in the Hamiltonian. Consider an isolated spin system with an initial Hamiltonian $\mathcal{H}_i$. At internal thermal equilibrium, the system can be characterized by a spin temperature β_i. Now, if we change the Hamiltonian suddenly to $\mathcal{H}_f$, after a time T_2 the system again attains internal equilibrium at a new temperature β_f. From Goldman,[25] we see that

$$\beta_f^{(\mathrm{sudden})} = \beta_i \frac{\mathrm{Tr}(\mathcal{H}_i \mathcal{H}_f)}{\mathrm{Tr}(\mathcal{H}_f^2)} . \tag{58}$$

If the process of changing $\mathcal{H}_i$ to $\mathcal{H}_f$ had been adiabatic instead of sudden, we would have preserved the spin order and obtained

$$\beta_I^{(\text{adiab})}=\beta_i\left[\frac{\text{Tr}(\mathcal{H}_i)^2}{\text{Tr}(\mathcal{H}_f)^2}\right]^{1/2} . \tag{59}$$

The loss of order due to a sudden change in the Hamiltonian can be characterized by a function f defined by

$$f\equiv\frac{\beta_f^{(\text{sudden})}}{\beta_f^{(\text{adiab})}}=\frac{\text{Tr}(\mathcal{H}_i\mathcal{H}_f)}{[\text{Tr}(\mathcal{H}_i)^2\,\text{Tr}(\mathcal{H}_f)^2]^{1/2}} . \tag{60}$$

Thus, if the Hamiltonian of an energy reservoir is suddenly changed, the resulting reciprocal spin temperature will be smaller by the factor f than it would have been if the change had been adiabatic.

Now consider the T_{1D}' pulse sequence (see Fig. 3). After the initial ADRF, $\vec{\text{H}}_{1I}$ is turned on suddenly at a frequency which is off resonance by an amount $\gamma_I h_1(\theta_I=\theta_{I1})$. Using ${}_D^{(0)}$ and ${}_D^{(00)}(\theta_{I1})$ as the initial and final Hamiltonians, respectively, we obtain from Eq. (60)

$$f=\frac{\text{Tr}[\mathcal{H}_D^{(0)}\mathcal{H}_D^{(00)}(\theta_{I1})]}{\{\text{Tr}[\mathcal{H}_D^{(0)}]^2\,\text{Tr}[\mathcal{H}_D^{(00)}(\theta_{I1})]^2\}^{1/2}} . \tag{61}$$

In evaluating the traces, we use the relation,

$$\mathcal{H}_D^{(0)}=\mathcal{H}_D^{(00)}(\theta_{I1})+\mathcal{H}_D^{(0n)}(\theta_{I1}) . \tag{62}$$

Since

$$\text{Tr}[\mathcal{H}_D^{(0n)}(\theta_{I1})H_D^{(00)}(\theta_{I1})]=0 , \tag{63}$$

we immediately obtain

$$f=\left[\frac{\text{Tr}[\mathcal{H}_D^{(00)}(\theta_{I1})]^2}{\text{Tr}[\mathcal{H}_D^{(0)}]^2}\right]^{1/2} . \tag{64}$$

If we neglect the effect of S spins (which is the case in our experiments when θ_{I1} is not near θ_m), we have

$$f=\tfrac{1}{2}(3\cos^2\theta_I-1) . \tag{65}$$

If we are very far from resonance ($\theta_I\cong 0$), we can see from this equation that $f\cong 1$. Thus, in the T_{1D}' pulse sequence, the step of turning on H_{1I} preserves dipolar order provided H_{1I} is far off resonance. Similarly, the step of turning H_{1I} off again yields the same result since Eq. (60) is symmetric in $\mathcal{H}_i$ and $\mathcal{H}_f$. In the experiments actually performed, $h_1=100$ G and $H_{1I}\cong 10$ G. Thus $\theta_{I1}\cong 6°$ and, from Eq. (65), $f=0.985$. So only 1.5% of the magnetization is lost by the sudden turn on of H_{1I}.

Another step in the T_{1D}' pulse sequence that needs closer examination is the sweeping of the $\vec{\text{H}}_{1I}$ frequency when the $\mathcal{H}_D^{(00)}$ reservoir is in a "cooled" state of dipolar order. Of course, as stated before, if the sweep rate is slow enough, the process is adiabatic and dipolar order is preserved. This requires that changes in $\mathcal{H}_D^{(00)}(\theta_I)$ occur sufficiently slowly that its reservoir can maintain internal thermal equilibrium at all times. For a system of strong I spins and weak S spins, this condition is most stringent at $\theta_I=\theta_m$ because of the absence at that angle of I-I interactions which normally bring the reservoir quickly to equilibrium.

This feature can be seen most easily from a calculation of the local field $H_{LI}(\theta_I)$ defined by

$$H_{LI}^2(\theta_I)=H_0^2\frac{\text{Tr}[\mathcal{H}_D^{(00)}(\theta_I)]^2}{\text{Tr}(\mathcal{H}_{ZI})^2} . \tag{66}$$

From the above expression, we calculated the local field in KF (I spins are ^{19}F, and S spins are ^{39}K) as a function of θ_I at two different crystal orientations (see Fig. 4). We can see that at $\theta_I\cong\theta_m$ the local field $H_{LI}(\theta_I)$ becomes very small, thereby resulting in a greatly lengthened time $T_2[\cong\gamma_I^{-1}H_{LI}^{-1}(\theta_I)]$ required for the $\mathcal{H}_D^{(00)}(\theta_I)$ reservoir to come to internal thermal equilibrium.

If we sweep θ_I slightly too fast to be completely adiabatic near θ_m, then the sweep can still be adiabatic outside some interval bounded by $\theta_I=\theta_m\pm\Delta\theta$. Over this interval, we can approximate the sweep by a sudden step in θ_I and use Eq. (60) to calculate the factor f:

$$f=\frac{\text{Tr}[\mathcal{H}_D^{(00)}(\theta_m-\Delta\theta)\,\mathcal{H}_D^{(00)}(\theta_m+\Delta\theta)]}{\{\text{Tr}[\mathcal{H}_D^{(00)}(\theta_m-\Delta\theta)]^2\,\text{Tr}[\mathcal{H}_D^{(00)}(\theta_m+\Delta\theta)]^2\}^{1/2}} . \tag{67}$$

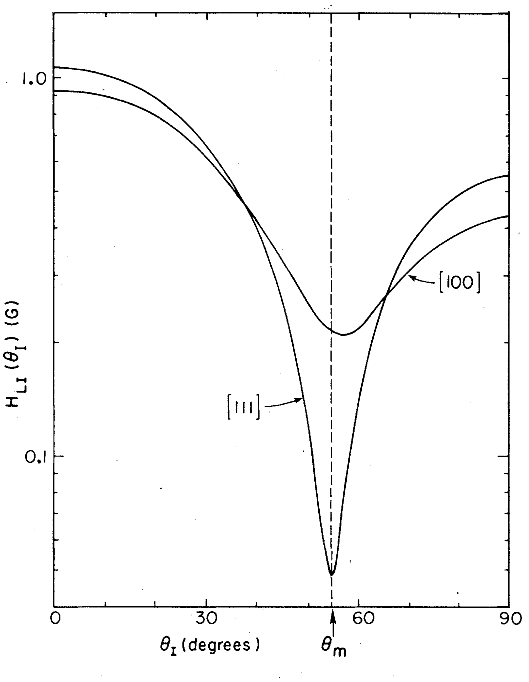

FIG. 4. The local field $H_{LI}(\theta_I)$ calculated from Eq. (66) for KF at two different crystal orientations: $\vec{\text{H}}_0$ along the [100] and [111] crystal axes as indicated in the figure.

If one uses Eqs. (20)–(22) for $\mathcal{H}_D^{(00)}(\theta_l)$, one should note that these expressions are written in a coordinate system with the z axis along $\vec{H}_{\text{eff}\,l}$ (which makes an angle θ_l with $\vec{H}_0$). Thus, the expressions for $\mathcal{H}_D^{(00)}(\theta_m-\Delta\theta)$ and $\mathcal{H}_D^{(00)}(\theta_m+\Delta\theta)$ would be in different coordinate systems. In calculating the trace in the numerator, it is important that the two dipolar interactions be written in the *same* coordinate frame. Thus, it is necessary to transform one of these terms to the coordinate frame of the other. We then obtain

$$f=\left[\left(\frac{3\cos^2(\theta_m-\Delta\theta)-1}{2}\right)\left(\frac{3\cos^2(\theta_m+\Delta\theta)-1}{2}\right)\left(\frac{3\cos^2(2\Delta\theta)-1}{2}\right)H_{LII}^2+\cos(\theta_m-\Delta\theta)\cos(\theta_m+\Delta\theta)\cos(2\Delta\theta)H_{LIS}^2\right]$$
$$\times\left[\left(\frac{3\cos^2(\theta_m-\Delta\theta)-1}{2}\right)^2H_{LII}^2+\cos^2(\theta_m-\Delta\theta)H_{LIS}^2\right]^{-1/2}\times\left[\left(\frac{3\cos^2(\theta_m+\Delta\theta)-1}{2}\right)^2H_{LII}^2+\cos^2(\theta_m+\Delta\theta)H_{LIS}^2\right]^{-1/2}. \quad (68)$$

Note that we neglected the S-S interactions. The third factor in each of the two terms in the numerator of Eq. (68) comes from the additional coordinate transformation described above. We calculated f for KF at two different crystal orientations (see Fig. 5).

For an adiabatic sweep ($\Delta\theta=0$), of course, we have $f=1$. As the sweep rate increases, $\Delta\theta$ increases and f decreases finally going negative. A negative f means that the spin temperature reverses its sign. In this case, the sign reversal is caused by the reversal in the direction of the local field during the nonadiabatic step so that spins aligned parallel to the local field before that step are now aligned antiparallel to the local field afterwards: hence a negative temperature. (Of course, the above treatment is valid only for the case of strong I spins and weak S spins.)

We verified this feature qualitatively with the following experiment. Instead of sweeping h at a constant rate in the T_{1D}' pulse sequence, we swept h from 100 to 15 G at a rate of 50 G/msec and then from 15 G to 2.5 G at some variable rate $\dot{h}$, and finally from 2.5 G to 0 at 50 G/msec. With this method, then, the sweep rate $\dot{h}$ over the region near the magic angle could be varied down to very small values. ($\theta_l=\theta_m$ corresponds to $h\cong 10$ G for this experiment.) The same sequence of sweep rates were applied in reverse to sweep h from 0 back up to 100 G again.

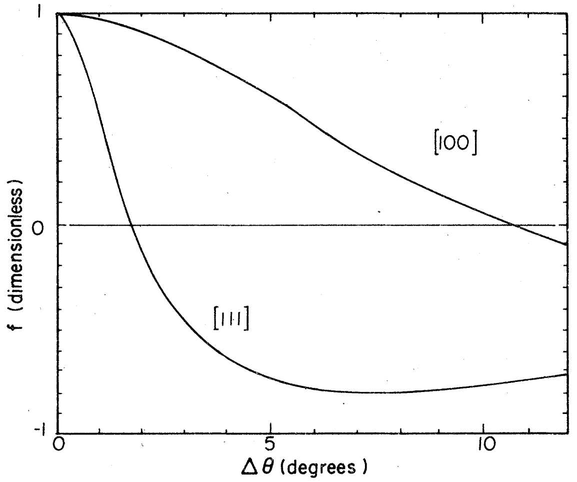

FIG. 5. The parameter f [defined by Eq. (60)] calculated from Eq. (68) for KF at two different crystal orientations: $\vec{H}_0$ along the [100] and [111] crystal axes as indicated in the figure.

The T_{1D}' pulse sequence, using the h-sweep described above, was applied to KF at room temperature ($\tau << T_{1D}'$) and the FID amplitude was measured as a function of $\dot{h}$ (see Fig. 6). Note that, in this experiment, we sweep θ_l through the magic angle twice (once in each direction); thus the resulting signal will be proportional to f^2. As we increase the sweep rate, f^2 should first decrease to zero and then increase to a positive value again. This is indeed what we observed (see Fig. 6). Note that we never quite attained complete adiabaticity in this experiment, even at $\dot{h}\cong 0.1$ G/msec. On the other hand, as can be seen in Fig. 6, we found that we could preserve much of the spin order by sweeping fast enough for f to be negative. Thus, in our T_{1D}' measurements, we used $\dot{h}\cong 80$ G/msec. Even though this sweep rate was far from being truly adiabatic, nevertheless, much of the spin order was preserved during the sweep. We thus have the surprising result that more signal is obtained if the sweep of θ_l is very nonadiabatic near θ_m than if it is almost adiabatic there. Of course, the sweep must be adiabatic for θ_l not near θ_m.

When using this technique, one must be particularly careful when measuring T_{1D}' near the magic angle. Small instabilities in the experimental apparatus can cause large effects. Earlier, we saw in AgF an apparent decrease in T_{1D}' near the magic angle, which we finally discovered was due to a droop in H_{1l} during the time interval τ of the T_{1D}' pulse sequence. Upon elimination of the droop in H_{1l}, the decrease in T_{1D}' disappeared.

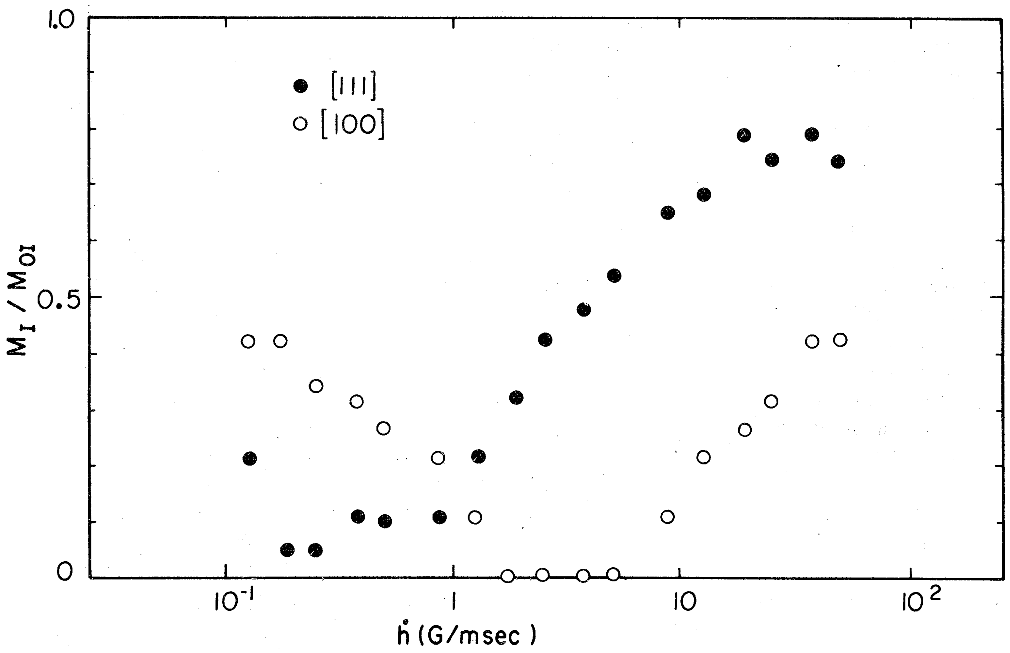

FIG. 6. M_I/M_{0I} as function of $\dot{h}$ in a T_{1D}' pulse sequence (described in the text) applied to KF at two different crystal orientations: $\vec{H}_0$ along the [100] and [111] crystal axes.

B. $T_{1\rho I}(\theta_I)$ pulse sequence

There are a variety of possible pulse sequences for measuring $T_{1\rho I}$ off resonance. We used a very simple sequence (see Fig. 7) which resembles a standard spin-locking technique commonly used for measuring $T_{1\rho}$ *on resonance.* The entire pulse sequence is applied at a single constant frequency off resonance. To insure a constant H_{1I}, we varied H_0 rather than ω_I in this experiment.

First we spin-lock the I spins by applying a pulse of length τ_p followed by a 90° phase shift. During the τ_p pulse, the I-spin magnetization $\vec{M}_I$ precesses about $\vec{H}_{\text{eff}\,I}$ with frequency $\gamma_I H_{\text{eff}\,I}$. After the 90° phase shift, $\vec{M}_I$ precesses about the new $\vec{H}_{\text{eff}\,I}$ until the perpendicular component dies to zero in a time of approximately T_2. Using simple geometric relationships, we calculate the "spin-locked" component of $\vec{M}_I$:

$$M_I^{(\mathrm{SL})} = M_{0I}[\sin^2\theta_I \sin(\gamma_I H_{\text{eff}\,I}\tau_p) + \cos\theta_I \sin^2\theta_I \cos(\gamma_I H_{\text{eff}\,I}\tau_p) + \cos^3\theta_I] \; . \tag{69}$$

Maximizing this equation with respect to τ_p, we find the length of pulse needed for spin-locking the maximum amount of magnetization:

$$\gamma_I H_{\text{eff}\,I}\tau_p = \cot^{-1}(\cos\theta_I) \; . \tag{70}$$

Putting this into Eq. (69), we obtain

$$M_I^{(\mathrm{SL})} = M_{0I}[\sin^2\theta_I(1+\cos^2\theta_I)^{1/2} + \cos^3\theta_I] \; . \tag{71}$$

This function has a minimum of $M_I^{(\mathrm{SL})} \cong 0.96 M_{0I}$ at $\theta_I \cong 55°$. Thus, by using the appropriate pulse length τ_p given by Eq. (70), nearly all of the original magnetization M_{0I} can be spin-locked along $\vec{H}_{\text{eff}\,I}$. One should note that a 90° phase shift is not the optimum for off-resonance spin-locking. However, as we have seen above, a 90° phase shift will result in a 96% magnetization even at the most unfavorable value for θ_I.

Following the spin-locking, $\vec{M}_I$ decays towards zero via spin-lattice relaxation and, after a time τ, is reduced by a factor $\exp[-\tau/T_{1\rho I}(\theta_I)]$. At this point, $\vec{H}_{1I}$ is turned off suddenly, and we observe the FID. [Actually, only the component of $\vec{M}_I$ perpendicular to $\vec{H}_0$

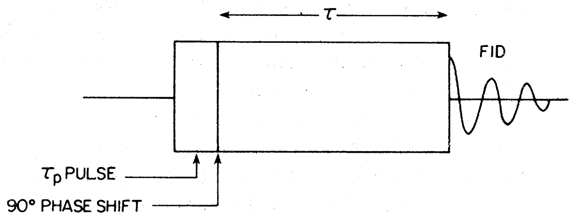

FIG. 7. Pulse sequence for measuring $T_{1\rho}(\theta_I)$. The entire sequence is done at a single frequency which is off resonance by an amount $h = H_{1I}\cot\theta_I$.

contributes to the FID and thus the maximum signal obtainable with this pulse sequence is approximately $M_0 \sin\theta_I$. In order to improve the efficiency for small θ_I (far off resonance), one should use a different pulse sequence such as the one described by Cornell and Pope.[36]]

IV. EXPERIMENTAL APPARATUS

We operated our NMR spectrometer at 24 MHz using a frequency synthesizer (Adret 6100 with plug-ins 6300 and 6500) which is remotely programmable. We swept frequency by using the "search mode" via an externally applied analog voltage.

Our probe was a single coil matched to 50 Ω. A combination of crossed diodes and quarter-wavelength transmission lines protected the receiver amplier during the rf pulse. We described a similar configuration in a previous paper.[13]

V. EXPERIMENTAL RESULTS

A. T_{1D} and $T_{1D}'(\theta_I)$

1. *Potassium fluoride (KF)*

In order to verify some of the theoretical expressions in Sec. II, we made T_{1D} and T_{1D}' measurements on a single crystal of KF (I spins are ^{19}F, S spins are ^{39}K) doped with about 1000-ppm mole fraction CaF$_2$. (This crystal was grown by the Crystal Growth Laboratory of the University of Utah Physics Department.) Similar crystals have been reported[11] to produce mobile potassium vacancies that dominate diffusion at low temperatures.

We measured the temperature dependence of T_{1D} (see Fig. 8) for KF at two different crystal orientations: $\vec{H}_0$ along the [100] and [111] crystal axes. In Fig. 8, we identify four different regions of relaxation processes. Region I ($T \gtrsim 170\,^\circ$C) is dominated by potassium diffusion as reported in Ref. 11. From the slopes of the lines through the data, we obtain activation energies $E_A = 0.75 \pm 0.15$ eV and 0.92 ± 0.15 eV for the [100] and [111] crystal orientations, respectively. These values are in fair agreement with that reported in Ref. 11 ($E_A = 0.83$ eV). (Note that, in drawing the solid lines in Fig. 8, we corrected the data by subtracting the relaxation rate due to the process dominant in Region II. Thus, the line represents the relaxation rate due to the Region I process alone, whereas the data itself is actually the sum of the relaxation rates of Region I *and* Region II processes.)

Our data (Fig. 8) for the two orientations shows that, in Region I, T_{1D} is very anisotropic, as predicted by Eq. (30) for S-spin diffusion. We made a more detailed anisotropy measurement at 227 °C (see Fig. 9). In this experiment, the crystal was oriented in $\vec{H}_0$ with the axis of rotation (perpendicular to $\vec{H}_0$) along the [110] crystal axis. Measurements of T_{1D} for various rotations are shown in Fig. 9. A theoretical calculation, using Eq. (30) which assumes S-spin diffusion, was made. In this calculation, the quantity $\tau/(1-p_{SI})$ was determined from a best fit to our data. (We treated the factor $(1-p_{SI})$ as being isotropic. Any error due to this approximation should be very small[20,21] compared to the effects which we study here.) Since there are no other adjustable parameters, the excellent agreement between theory and experiment in Fig. 9 is gratifying. The large anisotropy in T_{1D} verifies that diffusion of S spins is dominant at this temperature. Such a large anisotropy would not be observed if diffusion of I spins were dominant.

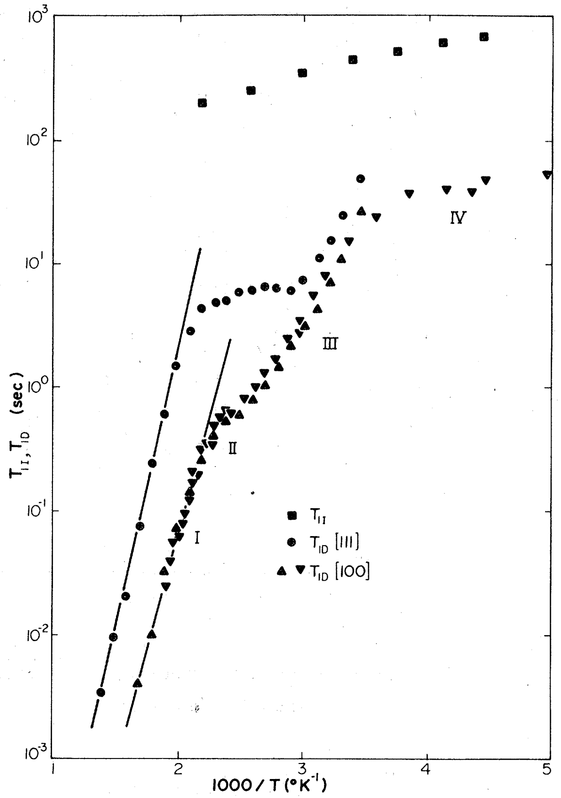

FIG. 8. T_{1I} and T_{1D} in KF at two different crystal orientations: $\vec{H}_0$ along the [100] and [111] crystal axes. The two different symbols for T_{1D} [100] refer to two different samples.

In Regions II and III of Fig. 8, the behavior of the data is very similar to that observed by Ho and Ailion[37,38] and also by Wei and Ailion[39,40] in various samples of doped CaF$_2$ and SrF$_2$. They interpreted the effect to be due to localized diffusion, i.e., mobile defects bound to impurity ions. Accordingly, it is likely that, in the present potassium fluoride T_{1D} data, we

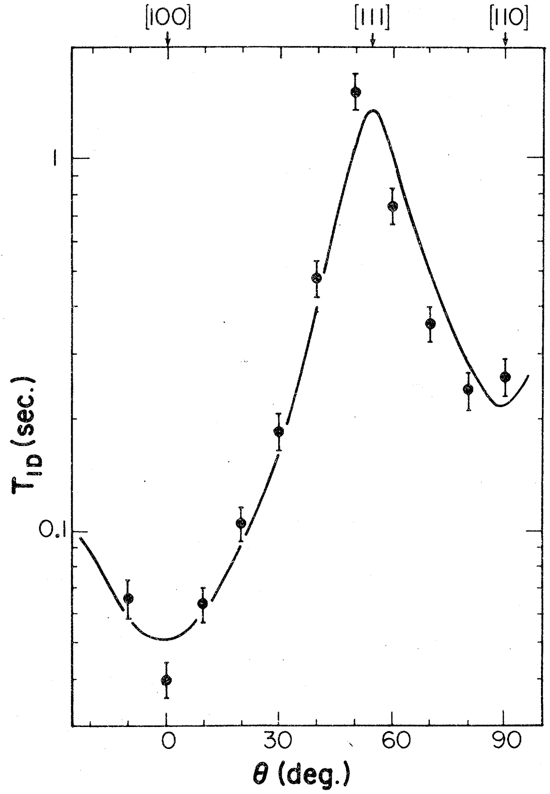

FIG. 9. T_{1D} anisotropy in KF at 227 °C. Crystal is rotated about its [110] axis.

see an effect also due to localized diffusion, that is, mobile potassium vacancies bound to Ca^{++} ions. Between Regions II and III, the slope of the data sharply decreases for increasing temperature. Wei and Ailion[39,40] showed evidence that this behavior was in their case caused by an abrupt change in diffusion mechanism. Thus the relaxation process of Region II and is not present in Region III, and the relaxation process of Region III is not present in Region II. Accordingly, the two relaxation rates do *not* add together in each other's region, in contrast to the case of Regions I and II discussed above. However, we are perplexed by the fact that the transition temperature between Regions II and III appears to change with crystal orientation.

From Fig. 8, we see that our Region II exhibits large anisotropy, as in Region I, which suggests that the dominant relaxation mechanism is some kind of potassium diffusion (possibly localized, as discussed above). Region III, on the other hand, exhibits much less anisotropy.

In Region IV ($T \lesssim 0$ °C), the relaxation rate seems to have very little temperature dependence and is possibly due to paramagnetic impurities. The T_{1l} data in Fig. 8 is probably due to paramagnetic impurity relaxation.

We chose to measure $T_{1D}'(\theta_l)$ as a function of θ_l at 200 °C (see Fig. 10). This temperature is in Region I of Fig. 8, where potassium diffusion dominates T_{1D}. At $\theta_l = 0$, the data point is actually a measurement of T_{1D}. Since $\mathcal{H}_D^{(00)}(\theta_l = 0)$ is equal to $\mathcal{H}_D^{(0)}$, a comparison of Eqs. (25) and (34) shows that $T_{1D}'(\theta_l = 0)$ is equal to T_{1D}. As predicted by Eq. (39) for S-spin motion, T_{1D}' shows a large dependence on θ_l (two orders of magnitude). A theoretical calculation of $T_{1D}'(\theta_l)$ using Eq. (39), fit to the value of T_{1D}' only at $\theta_l = 0$ (which is T_{1D}), is also shown in Fig. 10 and is in good agreement with the data. This data verifies an important feature of $T_{1D}'(\theta_l)$. By varying θ_l, we can vary the effect of S-spin diffusion on $T_{1D}'(\theta_l)$.

Measurements of $T_{1D}'(\theta_l)$ at $\theta_l = 90°$ ($h_2 = 0$) were also made as a function of temperature over part of Regions I and II (see Fig. 11). As can be seen, $T_{1D}'(90°)$ is much larger than T_{1D} (a feature characteristic of S-spin diffusion) and is thus in agreement with the anisotropy measurements which similarly demonstrate that S-spin diffusion is dominant.

2. *Silver fluoride (AgF)*

T_{1D} and $T_{1D}'(90°)$ were also measured[12,23] in two different samples of AgF. Sample No. 1 was obtained from Research Organic/Inorganic Chemical Corp. (AG-10, 98% pure) and Sample No. 2 from Cerac/Pure Inc. (S-1080, 99.5% pure). [A third sam-

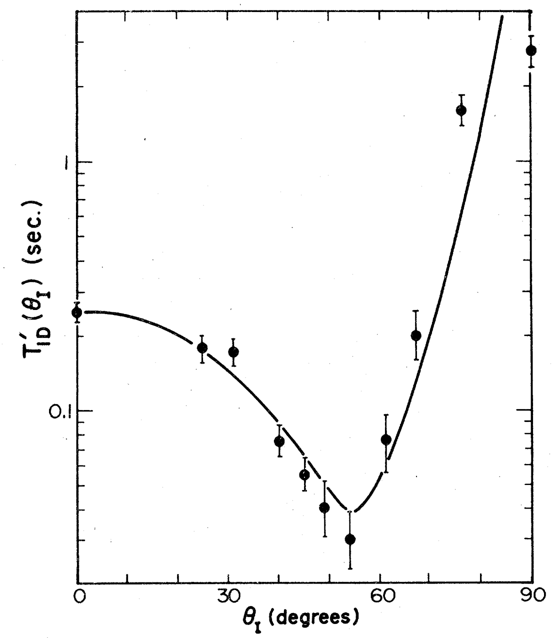

FIG. 10. T_{1D}' as a function of θ_l in KF at 200 °C. Note that the data point at $\theta_l = 0$ is T_{1D}.

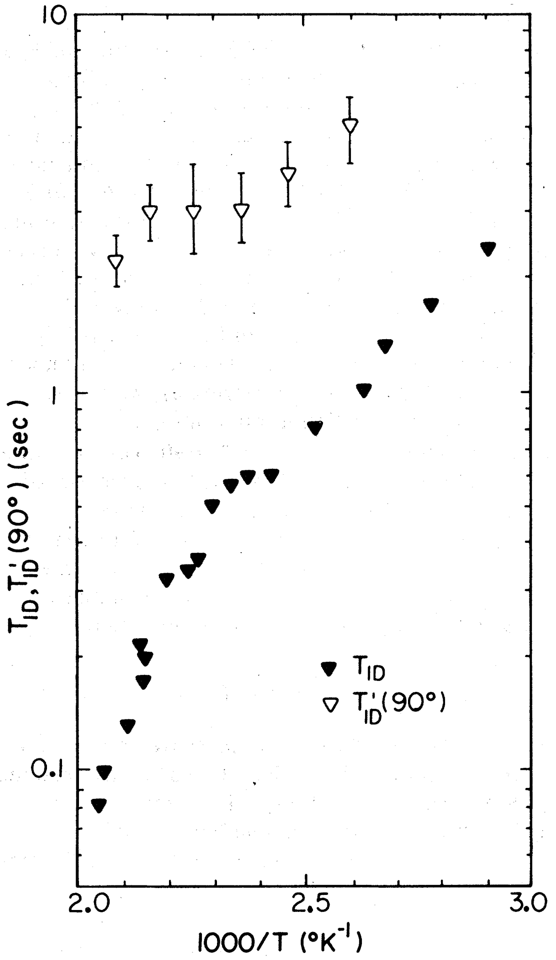

FIG. 11. T_{1D} and $T_{1D}'(90°)$ in KF with $\vec{H}_0$ along the [100] crystal axis.

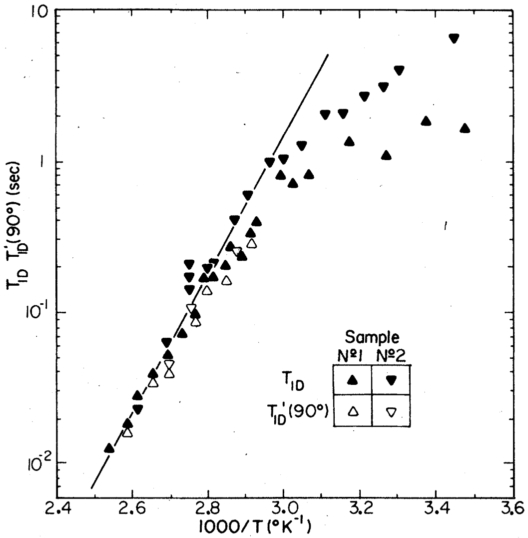

FIG. 12. T_{1D} and $T_{1D}'(90°)$ in two different samples of AgF.

ple was obtained from Apache Chemicals Inc. (#6957, 99% pure) but apparently contained too much magnetic impurity for useful data to be obtained.] To our knowledge, no previous diffusion measurements have ever been made in AgF. From the temperature dependence of T_{1D} (see Fig. 12), some motional process is evident at temperatures above $T \cong 60\,°\text{C}$. Note that data from both samples are plotted in Fig. 12 and that they behave similarly in this diffusion region. At lower temperatures, where paramagnetic impurities possibly dominate T_{1D}, they differ significantly with the purer sample (Sample No. 2) having the longer relaxation time. From the slope of the line drawn through the data points, we obtain $E_A = 0.92 \pm 0.15$ eV. As in KF, the data was corrected by subtracting off the relaxation rate of the low-temperature process.

Actually, AgF is a three-spin system: ^{19}F, ^{107}Ag, and ^{109}Ag. Labeling ^{19}F as the I spins, and the two silver isotopes as S spins, the theoretical expressions given in Sec. II need be only slightly modified. Since the interactions between the S spins are so small that they can be neglected, the effect of S-spin motion on relaxation rates can be calculated separately for ^{107}Ag and ^{109}Ag and then added together to obtain the net relaxation rate.

We measured $T_{1D}'(\theta_l)$ for $\theta_l = 90°$ over the entire temperature region where diffusion dominates. In Fig. 12, we see that $T_{1D}'(90°) = T_{1D}$ for both samples. This behavior is typical of I-spin diffusion [see Eq. (37)], as contrasted with the behavior, $T_{1D}'(90°) >> T_{1D}$, characteristic of S-spin diffusion (see Fig. 11). Thus, we have conclusive evidence that fluorine diffusion dominates T_{1D} in our samples of AgF.

We also measured $T_{1D}'(\theta_l)$ as a function of θ_l in both samples (see Figs. 13 and 14). As can be seen from this data, $T_{1D}'(\theta_l)$ is approximately independent of θ_l. Again, this is behavior typical of I-spin diffusion [see Eq. (37)], in contrast to that of S-spin diffusion seen in Fig. 10. [We have not attempted to explain the slight decrease in $T_{1D}'(\theta_l)$ for increasing θ_l.]

S-spin diffusion has the greatest effect on $T_{1D}'(\theta_l)$ when θ_l is near θ_m. In Fig. 13, for example, we see that at $\theta_l = 52°$ (which is near θ_m), $T_{1D}'(\theta_l)$ approximately equals T_{1D} and is therefore dominated by I-spin diffusion. At this angle ($\theta_l = 52°$), $T_{1D}'(\theta_l)$ due to S-spin diffusion in AgF is given by [see Eq. (39)]

$$\frac{1}{T_{1D}'(52°)} = (0.47)\frac{1}{\tau_S}(1 - p_{SI}) \quad . \tag{72}$$

The fact that I spin diffusion dominates $T_{1D}'(52°)$

means that the relaxation rate given by Eq. (37) for I-spin diffusion must be much larger than that given by Eq. (72) above for S-spin diffusion. Thus, assuming that $2(1-p_{II})$ and $(1-p_{SI})$ are of the same order of magnitude, we conclude that, for this sample of AgF, $\tau_I \ll \tau_S$.

In all of the other silver halides (AgCl,AgBr,AgI), silver diffusion is dominant.[41,42] Hence, it was somewhat surprising to us to find that in AgF fluorine diffusion is dominant. Perhaps one factor influencing this behavior is the impurities in AgF. In contrast to the other silver halides, high-purity samples of AgF are not available. AgF is also very reactive and usually contains a considerable amount of AgF_2 and Ag_2F.[43] Impurities in AgF could increase significantly the number of mobile fluorine defects, thus causing fluorine diffusion to be dominant.[37-40]

B. $T_{1\rho I}(\theta_I)$

We measured $T_{1\rho I}$ on resonance ($\theta_I = 90°$) in KF ([100] crystal orientation) as a function of temperature (see Fig. 15). From the slope of the line, we obtain $E_A = 0.76 \pm 0.15$ eV, in agreement with that of Region I in Fig. 8. Thus potassium vacancy diffusion dominates $T_{1\rho I}$ over this temperature region. At 351 °C, we made one $T_{1\rho I}$ measurement for the [111] orientation and found a large anisotropy. From calcu-

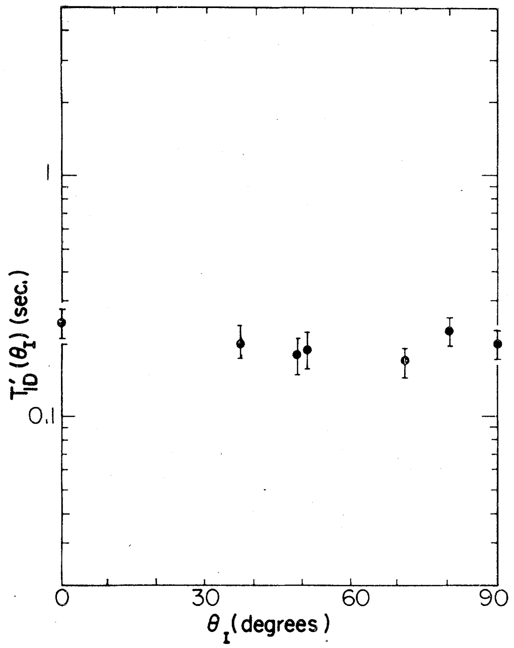

FIG. 13. T_{1D}' as a function of θ_I in Sample No. 1 of AgF at 68 °C. Note the data point at $\theta_I = 0$ is T_{1D}.

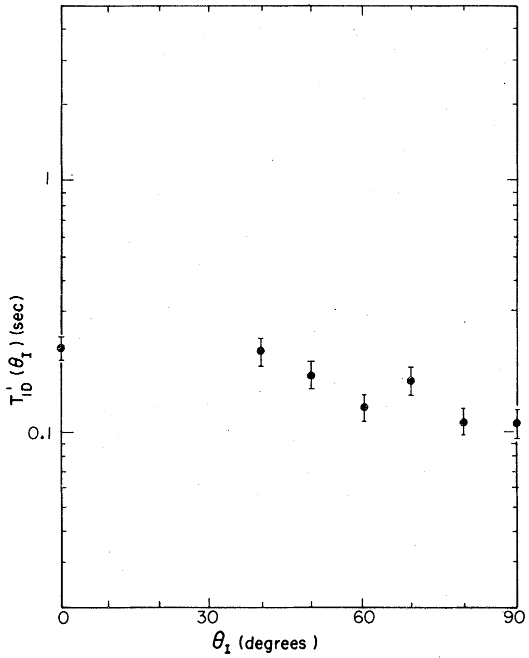

FIG. 14. T_{1D}' as a function of θ_I in Sample No. 2 of AgF at 89 °C. Note the data point at $\theta_I = 0$ is T_{1D}.

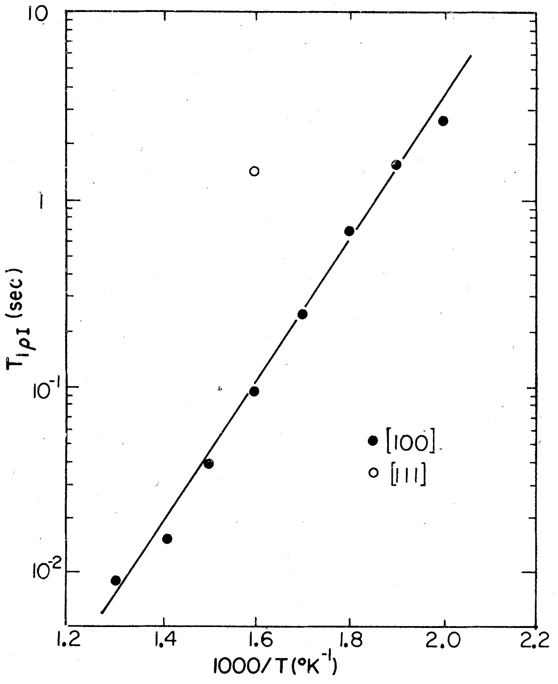

FIG. 15. $T_{1\rho I}$ on resonance ($\theta_I = 90°$) in KF at two different crystal orientations: $\vec{H}_0$ along the [100] and [111] crystal axes.

lations of $J^{(0)}(\omega)$ found in the literature,[9,33] we find that the theoretical anisotropy is

$$\frac{T_{1\rho I}([111])}{T_{1\rho I}([100])} = \begin{cases} 0.65, & I\text{—spin diffusion} \\ 26, & S\text{—spin diffusion} \end{cases}$$

Thus, the $T_{1\rho I}$ anisotropy measured in KF also clearly verifies that, in this region, potassium diffusion dominates $T_{1\rho I}$.

$T_{1\rho I}(\theta_I)$ was measured in KF at 351 °C as a function of θ_I. The ratio $T_{1\rho I}(\theta_I)/T_{1\rho I}(90°)$ is plotted in Fig. 16 along with the theoretical calculation from Eq. (53) for S-spin diffusion. To contrast this case with that of I-spin diffusion, $T_{1\rho I}(\theta_I)$ was measured in a single crystal of undoped CaF_2 at 314 °C. (I spins are ^{19}F. There are no S spins of any significance.) At this temperature, fluorine diffusion dominates $T_{1\rho I}$. (We concluded this by measuring $E_A \cong 0.9$ eV and comparing it with the other measurements.[39,40])

The ratio $T_{1\rho I}(\theta_I)/T_{1\rho I}(90°)$ is plotted in Fig. 16 along with the theoretical calculation from Eq. (52) for I-spin diffusion. As can be seen in Fig. 16, agreement between data and theory is fairly good, especially the contrast between I-spin and S-spin diffusion. It is clear that these measurements provide an easy method for distinguishing between the two types of diffusion.

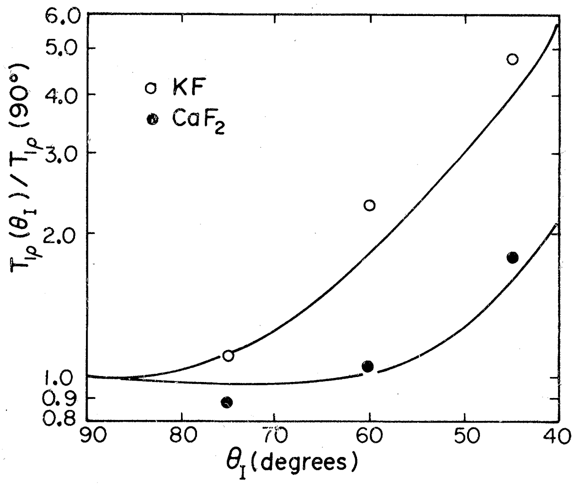

FIG. 16. The ratio $T_{1\rho}(\theta_I)/T_{1\rho}(90°)$ in KF in the [100] orientation at 351 °C and in CaF_2 in the [111] orientation at 314 °C. The upper and lower curves are calculated from Eqs. (53) and (52), respectively.

VI. CONCLUSIONS

In this paper, we have described some new methods for identifying and studying the diffusing species in multispin systems. We have demonstrated that anisotropy measurements of T_{1D} and $T_{1\rho}$ for a two spin system of strong I and weak S spins is clearly capable of distinguishing between diffusion of the two species. Anisotropy measurements may similarly be useful in other types of multispin systems (e.g., strong I and strong S spins as in LiF). Of course, such anisotropy measurements are limited to systems in which single crystals are obtainable.

We introduced a new technique involving a new relaxation time T_{1D}' which also can be very effective in distinguishing between diffusion of different spin species. This technique has the advantage that it is not restricted to single crystals and can easily be applied to polycrystalline samples. Furthermore, we have shown that T_{1D}' measurements can enhance substantially the effects of the diffusion of weak spins. Not only can this technique be applied to the study of abundant weakly magnetic spins (as in the cases described in this paper) but almost certainly it can be extended to the case of diffusion of dilute strongly magnetic spins (e.g., diffusing impurities). Our technique also has the capability of allowing us to separate competing diffusion processes and study them individually.

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