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Nature of Ag^+ self-diffusion in AgF

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Measurements of the nuclear magnetic resonance (NMR) dipolar relaxation times T_{1D} and $T_{1D'}$ (51°) have been made on the ^{19}F resonance in AgF powder over the temperature range 60–300 K. Also the technique of Stokes and Ailion for detecting the diffusion of weakly magnetic spins has been verified for powder samples by measuring $T_{1D'}(\theta_l)$ vs θ_l in KF: 0.1 at. % CaF_2 powder. A comparison of the NMR results with conductivity measurements of Raaen, Svare, and Fjeldly allows one to rule out diffusion mechanisms in AgF which give rise to strong-collision NMR relaxation, like Ag^+ vacancy or Ag^+ interstitialcy diffusion in AgF, thereby suggesting the dominance of a weak-collision mechanism like Ag^+ interstitial or possibly grain-boundary diffusion.

An interesting question involves the determination of microscopic details concerning the nature of ionic diffusion in solids. In particular, it is important to determine the nature of the diffusing species, the jump mechanism, and the site symmetry. Since ionic conductivity and nuclear magnetic resonance (NMR) both are sensitive to atomic diffusion but measure different parameters (conductivity and relaxation time, respectively), a comparison of the two can result in insight into the diffusion process.

Recently, Raaen *et al.*[1] measured the spin-lattice relaxation time T_1 and the rotating-frame relaxation time $T_{1\rho}$ for ^{19}F relaxation in AgF powder over the temperature range 120–500 K. In an earlier paper Stokes and Ailion[2] also studied ^{19}F relaxation in AgF in the temperature range 300–400 K by measuring the dipolar relaxation time both in the lab frame (T_{1D}) and in the rotating frame ($T_{1D'}$). These studies were in agreement in that they both observed a fluorine motional contribution to the relaxation but observed *no* contribution to the measured relaxation times arising from Ag^+ diffusion. However, Raaen *et al.* did report a large electrical conductivity, which is almost certainly due to the motion of Ag^+ ions. From their conductivity data, one can estimate a value for the mean atomic jump time τ which in turn should result in ^{19}F NMR relaxation-time minima at lower temperatures due to the motion of the Ag^+ ions. The failure of Raaen *et al.* to see these motions suggests that the ^{19}F relaxation effects due to the Ag^+ motion are sufficiently weak that they are masked by other relaxation mechanisms.

In order to see motional effects due to the Ag^+ ions, we extended the T_{1D} measurements of Stokes and Ailion down to 60 K. (Using Raaen *et al.*'s conductivity results of 0.2 eV for activation energy and an attempt frequency of 30×10^{11} for noncollinear interstitialcy jumps,[3] we estimated that the T_{1D} minimum due to Ag^+ motion should occur at approximately 120 K. If, on the other hand, we used Raaen *et al.*'s value of 4×10^9 cm^2/sec for D at room temperature, we would predict that the T_{1D} minimum should be at approximately 150 K.) As can be seen in Fig. 1, our T_{1D} data show no sign of any diffusion over the entire region.

Stokes and Ailion[2] showed that it is possible to enhance relaxation effects due to motions of weakly magnetic spins by measuring the rotating-frame dipolar relaxation time $T_{1D'}$. This relaxation time depends upon the angle θ_l between the rotating-

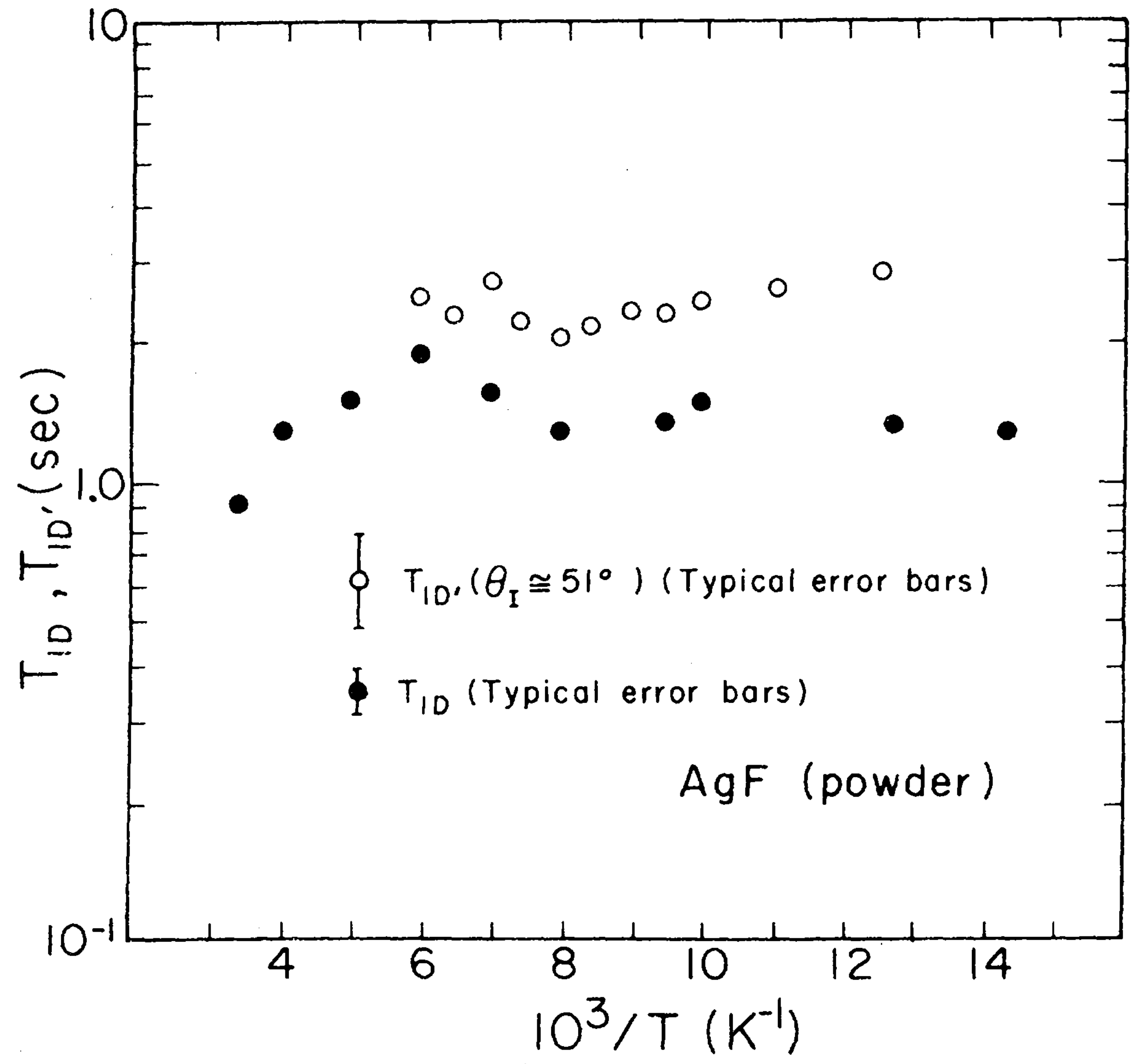

FIG. 1. T_{1D} and $T_{1D'}(\theta_l \cong 51°)$ vs $1/T$ in AgF powder.

frame effective field and the z-direction where

$$\theta_l = \tan^{-1}\left(\frac{H_1}{H_0-\omega/\gamma}\right) . \tag{1}$$

This enhancement is a maximum at the "magic angle" (54.7°), at which $\cos^2\theta_l = 1/3$. The temperature change of the system due to motions of the weak spins (S spins) is a maximum at this angle, since the heat capacity of the strong (I-I) interaction equals zero[2] when $\cos^2\theta_l = 1/3$. It is thus possible that, even though T_{1D} may not be sensitive to the motion of the S spins, $T_{1D'}$ measured near the magic angle ($\theta_m = 54.7°$) could still reflect the diffusion of the S spins. In this case, a temperature plot of $T_{1D'}(\theta_m)$ would exhibit a diffusion minimum. On Fig. 1, we have also plotted our measurements of $T_{1D'}$ (at $\theta_l \cong 51°$) over the entire temperature range. (It should be pointed out that, since the $T_{1D'}$ relaxation is nonexponential both in this figure and in Fig. 2, we determine $T_{1D'}$ in both cases from the initial rates of decay. In AgF the nonexponentiality is due to the fact that the relaxation time is highly anisotropic in a powder. There is no difficulty in detecting diffusion by this procedure since all portions of the relaxation should experience the same activation energy and thus should exhibit the same temperature dependence.) As can be seen, neither the $T_{1D'}$ nor the T_{1D} measurements show any evidence of the diffusion mechanism which is responsible for Raaen *et al.*'s conductivity data.

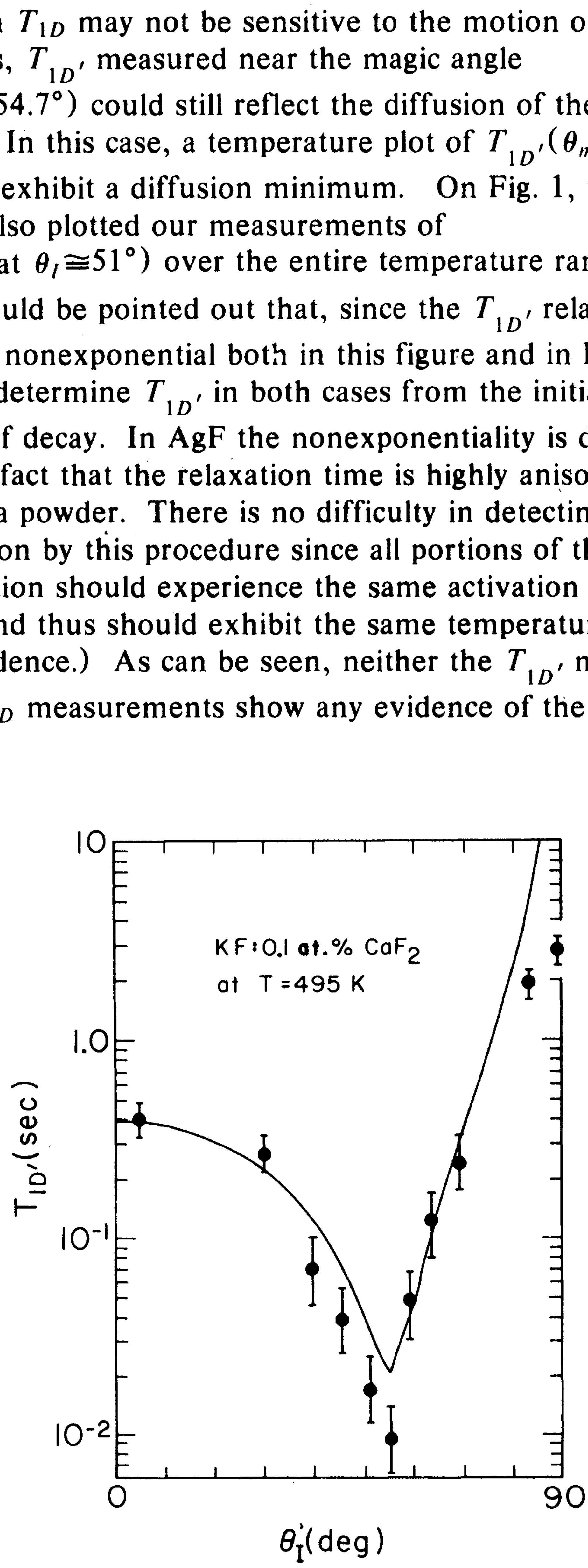

FIG. 2. $T_{1D'}$ vs θ_l at $T=495$ K in powdered KF doped with 0.1 at.% CaF$_2$. The solid curve is calculated from Eq. (2) and is fitted to the data only at one point, $T_{1D'}(\theta_l=0) \equiv T_{1D}$.

It is interesting to note the somewhat curious fact that $T_{1D'}$ is longer than T_{1D}, in contrast to what one would expect for diffusion of weakly magnetic spins. This phenomenon can be understood by realizing that, in $T_{1D'}$ near the magic angle, I-I dipolar interactions are strongly reduced. If the relaxation is due to paramagnetic ions whose effects are quickly communicated to the bulk spins via I-I spin diffusion, the reduction of I-I interactions will inhibit this spin diffusion[4] and result in a longer relaxation time, as we have observed.

At this point we should note that, even though the $T_{1D'}$ method of Stokes and Ailion is *believed* to be valid for powder as well as single-crystal samples, it was *verified* experimentally by them only for a single crystal. Since our AgF sample is a powder, we felt it to be imperative that we verify that the method of Stokes and Ailion is indeed valid for a powder sample in which the diffusion of weakly magnetic spins is known to be dominant.

Accordingly, we measured $T_{1D'}$ vs θ_l in a powder sample of KF:0.1 at.% Ca^{++} in which the motion of K$^+$ vacancies is known[2,5] to dominate the diffusion at low temperatures. Equation (2) is the formula, originally derived by Stokes and Ailion,[2] for the dependence of $T_{1D'}$ on θ_l for diffusion of weak (S) spins:

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

In this equation, the principal terms which depend on crystal orientation and thus which must be averaged for a powder are the local fields H_{LII}^2, H_{LIS}^2, and H_{LSS}^2. (Since the terms $1-p_{SI}$ and $1-p_{SS}$ are geometrical factors of order unity whose angular variation is less than 20% typically,[6] we simplified our calculation by replacing each term by 1.) Figure 2 shows a plot of the θ_l dependence for our calculated powder average $\langle 1/T_{1D'}\rangle^{-1}$ as well as our experimental measurements of $T_{1D'}$ for KF:0.1 at. % Ca^{++} at 222 °C. The general agreement between the theoretical curve and experimental points confirms the validity of the Stokes-Ailion method for observing the diffusion of weakly magnetic spins in a powder sample. It should be noted that, in AgF, $T_{1D'}$ exhibits no such dependence[2] on θ_l. (The fact that our experimental points lie somewhat below the theoretical curve near the magic angle is probably due to the difficulty in satisfying the adiabatic condition for very short relaxation times.)

With regard to AgF, how do we account for the failure of Ag$^+$ diffusion to be manifested either in the T_{1D} or in the $T_{1D'}$ data? Why should there be such a large contribution to the conductivity and yet no contribution to the NMR relaxation times T_{1D} and $T_{1D'}$? Our proposed explanation sheds some light on the microscopic nature of the Ag^+ diffusion in AgF. It should be noted that the theories which predict deep relaxation minima in T_{1D} and $T_{1D'}$ are strong-collision theories[7] which assume that a significant loss in dipolar order per atom results from each atomic diffusion jump. Such theories would be applicable to the low-temperature sides of relaxation minima for processes, such as vacancy or interstitialcy diffusion, in which each lattice atom of a given species jumps on the average once every τ. On the other hand, if the mechanism were interstitial diffusion involving jumps of interstitial atoms but not of lattice atoms, the NMR results would be strikingly different, even though the ionic conductivity would not be significantly affected. For interstitial diffusion, we must distinguish two kinds of atoms of a given species, the interstitial atoms and lattice atoms. The bulk of the NMR signal would come from the immobile lattice atoms which would be relaxed only weakly by the moving interstitial atoms. Interstitial diffusion is a weak-collision mechanism for the stationary lattice atoms since only a *fraction* of each lattice atom's dipolar energy changes in an interstital jump (i.e., the interaction between the lattice atom and the interstitial atom changes but the interaction between the lattice atom and all other lattice atoms remains unchanged). In contrast, in vacancy or interstitialcy diffusion the lattice atom jumps and its interaction energy with *all* other atoms changes. Accordingly, interstitial diffusion would result in very weak NMR relaxation minima which could easily be masked by other relaxation mechanisms. (Another possible mechanism which could contribute to the conductivity but not appreciably to the NMR relaxation would be grain-boundary diffusion[8] which also would involve only a small fraction of the Ag^+ atoms but may have a lower activation energy than normal bulk diffusion.) If we consider that, in addition to this weak-collision silver diffusion, there exists a less-frequent strong-collision mechanism such as vacancy or interstitialcy diffusion, then our failure to see the latter's effect on $T_{1D'}$ allows us to place a lower limit on its frequency. Since $T_{1D'} \sim \tau_S$ at the magic angle,[2] our failure to see relaxation effects due to diffusion implies that τ_S due to strong-collision mechanisms must be longer than ~2 sec at all temperatures in our study.

It is interesting to note that our conclusions for AgF contrast with what is thought to occur in other silver halides. Weber and Friauf[3] concluded from correlation-factor studies that the dominant intrinsic diffusion mechanism in AgCl and AgBr is the silver interstitialcy mechanism. If we use their activation energy (~0.8 eV) and attempt frequency ($\sim 10^{12}-10^{13}$ Hz), we would predict a T_{1D} minimum due to this mechanism to occur at about 400 K. This temperature is in the range, investigated by Raaen *et al.*[1] and Stokes and Ailion,[2] in which no strong-collision effects due to Ag^+ motion were observed. Normally, one would expect[9] that the direct interstitial mechanism would have a large activation energy. However, more recent theoretical studies[10] indicate that the quadrupolar deformability of the Ag^+ ion leads to a reduction in the transverse-optical-phonon frequencies and the elastic constant C_{44} which in turn will reduce the activation energies for Ag^+ diffusion by several tenths of an eV. This effect may cause the interstitial mechanism to be more favored in AgF than in AgCl and AgBr.

Our principal conclusion then is that the dominant diffusion mechanism over the range 60–300 K in AgF cannot be Ag^+ vacancy or interstitialcy diffusion, but is rather a weak-collision mechanism like Ag^+ interstitial or grain-boundary diffusion. Furthermore, we have seen that a comparison of NMR and conductivity measurements can allow interstitial diffusion to be distinguished from a strong-collision mechanism such as vacancy or interstitialcy diffusion.

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