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# Cross Relaxation in LiF*

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A combined experimental and theoretical study of cross relaxation in LiF has been carried out. In agreement with theory, the cross-relaxation time $T_{21}$ is observed to be strongly anisotropic and field dependent; at 51.7 gauss it goes from 0.025 second in the [100] direction to 7 seconds in the [111] direction. A frequency distribution function analogous to the line shapes for magnetic absorption is measured down to $10^{-4}$ times the maximum value; for most orientations a Gaussian is an excellent approximation to it.

## I. INTRODUCTION

ABRAGAM and Proctor[1] demonstrated that two spins with different resonance frequencies can exchange energy and come into thermal equilibrium with each other, independent of the lattice, if the difference in their resonant frequencies is comparable to the local fields. This is cross relaxation and Bloembergen, Shapiro, Pershan, and Artman[2] (BSPA) have given a theory to explain this and several other experiments.[3–7]

In this paper the cross-relaxation process in LiF is examined in great detail and a quantitative comparison with theory is made. Cross relaxation can only be detected when different spins exchange energy with one another faster than they exchange energy with the lattice; because the spin-lattice relaxation times in LiF are a few minutes, the cross-relaxation time $T_{21}$ can be measured over three decades as a function of magnetic field and crystal orientation.

The theory presented in Sec. II is an extension of previous work.[8] in which the author predicted large anisotropies in $T_{21}$. The experiment, similar to Abragam and Proctor's $T_{21}$ measurement, is discussed in detail in Sec. III. In Sec. IV we discuss the results and show that for some crystal orientations the absorption lines in LiF can be approximated by a single Gaussian function.

## II. THEORY

### A. Transition Probability

The simplest cross-relaxation process is when two spins, one Li and one F, make simultaneous opposite flips, the unbalance in Zeeman energy being taken up by the dipole-dipole interaction. For simplicity, we will start with this case although BSPA have shown this is not the mechanism for cross relaxation in LiF at fields above 50 gauss. Assume $\text{Li}^7$ is 100% abundant, although it is actually 92.6%,[9] and ignore its quadrupole moment; in a perfect cubic crystal there should not be a quadrupole interaction and the defects that cause one in a real crystal can be neglected in this experiment. Also assume a rigid lattice with infinite spin-lattice relaxation time $T_1$; the effect of finite $T_1$ will be added later.

The Hamiltonian for the system can be written as:

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_2, \tag{1}$$

where $\mathcal{H}_0$ is the Zeeman terms, $\mathcal{H}_1$ is that part of the dipole-dipole interaction that commutes with the Zeeman terms, and $\mathcal{H}_2$ is the rest of the dipole-dipole interaction. $\mathcal{H}_0+\mathcal{H}_1$ is the truncated Hamiltonian that Van Vleck[10] retains in his moment calculations and $\mathcal{H}_2$ is the nondiagonal terms he discards. If we denote a lithium spin operator by $S$, a fluorine spin operator by $I$, and if one prime refers to an interaction between a lithium and a fluorine, two primes to one between two fluorines and no prime between two lithiums, then using the notation of BSPA $\mathcal{H}_1$ and $\mathcal{H}_2$ are given as:

$$\begin{aligned}\mathcal{H}_1&=A+B+A'+A''+B'',\\ \mathcal{H}_2&=B'+C+C'+D'+E+(B'+C+C'+D'+E)^\dagger\\ &\qquad+\text{other terms of no importance,}\end{aligned} \tag{2}$$

where

$$A=\sum_{i,j}A_{ij}S_{zi}S_{zj}:\qquad A_{ij}=-\frac{1}{2}\frac{\gamma_{\text{Li}}^2\hbar^2}{r_{ij}^3}(1-3\cos^2\theta_{ij}),$$

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[1] A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).

[2] Bloembergen, Shapiro, Pershan, and Artman, Phys. Rev. **114**, 445 (1959).

[3] Robert T. Schumacher, Phys. Rev. **112**, 837 (1958).

[4] H. S. Gutowsky and D. E. Woessner, Phys. Rev. Letters ,1 6 (1958).

[5] Walter I. Goldburg, Bull. Am. Phys. Soc. 4, 165 (1959).

[6] S. Shapiro and N. Bloembergen, Phys. Rev. **116**, 1453 (1959).

[7] Sorokin, Lasher, and Gelles, *Proceedings of the Conference on Quantum Electronics, Bloomingberg, New York, 1959.*

[8] P. S. Pershan, Bull. Am. Phys. Soc. 4, 165 (1959).

[9] *Handbook of Chemistry and Physics,* edited by C. D. Hodgman (Chemical Rubber Publishing Company, Cleveland, 1954–1955), p. 394.

[10] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

$$A'=\sum_{i,j} A_{ij}'S_{zi}I_{zj}: \qquad A_{ij}'=\frac{\gamma_{\mathrm{Li}}\gamma_{\mathrm{F}}\hbar^2}{r_{ij}^3}(1-3\cos^2\theta_{ij}),$$

$$A''=\sum_{i,j} A_{ij}''I_{zi}I_{zj}: \qquad A_{ij}''=\frac{1}{2}\frac{\gamma_{\mathrm{F}}^2\hbar^2}{r_{ij}^3}(1-3\cos^2\theta_{ij}),$$

$$B=\sum_{i,j} B_{ij}(S_{+i}S_{-j}+S_{-i}S_{+j}): \qquad B_{ij}=-\frac{1}{8}\frac{\gamma_{\mathrm{Li}}^2\hbar^2}{r_{ij}^3}(1-3\cos^2\theta_{ij}),$$

$$B'=\sum_{i,j} B_{ij}'S_{+i}I_{-j}: \qquad B_{ij}'=-\frac{1}{4}\frac{\gamma_{\mathrm{Li}}\gamma_{\mathrm{F}}\hbar^2}{r_{ij}^3}(1-3\cos^2\theta_{ij}),$$

$$B''=\sum_{i,j} B_{ij}''(I_{+i}I_{-j}+I_{-i}I_{+j}): \qquad B_{ij}''=-\frac{1}{8}\frac{\gamma_{\mathrm{F}}^2\hbar^2}{r_{ij}^3}(1-3\cos^2\theta_{ij}),$$

$$C=\sum_{i,j} C_{ij}(S_{zi}S_{+j}+S_{+i}S_{zj}): \qquad C_{ij}=-\frac{3}{4}\frac{\gamma_{\mathrm{Li}}^2\hbar^2}{r_{ij}^3}\sin\theta_{ij}\cos\theta_{ij}e^{-i\phi_{ij}},$$

$$C'=\sum_{i,j} C_{ij}'S_{+i}I_{zj}: \qquad C_{ij}'=-\frac{3}{2}\frac{\gamma_{\mathrm{Li}}\gamma_{\mathrm{F}}\hbar^2}{r_{ij}^3}\sin\theta_{ij}\cos\theta_{ij}e^{-i\phi_{ij}},$$

$$D'=\sum_{i,j} D_{ij}'S_{zi}I_{-j}: \qquad D_{ij}'=-\frac{3}{2}\frac{\gamma_{\mathrm{Li}}\gamma_{\mathrm{F}}\hbar^2}{r_{ij}^3}\sin\theta_{ij}\cos\theta_{ij}e^{+i\phi_{ij}},$$

$$E=\sum_{i,j} E_{ij}S_{+i}S_{+j}: \qquad E_{ij}=-\frac{3}{8}\frac{\gamma_{\mathrm{Li}}^2\hbar^2}{r_{ij}^3}\sin^2\theta_{ij}e^{-2i\phi_{ij}}.$$

The terms $A$, $B$ and $A''$, $B''$, etc., are half of their usual values because we choose to sum over each interaction twice.

Consider the following hypothetical experiment. Initially the lithium spin system is at an infinite spin temperature, and the fluorine system is at room temperature in a field of 5000 gauss. Without changing direction, the field is suddenly dropped to $H_0$, of the order of 50 gauss say, and stays there for a time $t$ when it is raised back to 5000 gauss, again without changing direction. It can be shown[8] that this is equivalent to turning on $\mathcal{H}_2$ for a time $t$, as in text book examples of standard time-dependent perturbation theory.[11] Treating $\mathcal{H}_2$ by this method, we find the probability per unit time that one lithium "$i$" and one fluorine "$j$" have simultaneously flipped is given by

$$W_{m_{\mathrm{Li}}\to m_{\mathrm{Li}}+1;\, m_{\mathrm{F}}\to m_{\mathrm{F}}-1}=\frac{2\pi}{\hbar^2}g_{12}(\omega_{12})|B_{ij}'|^2 \times|\langle m_{\mathrm{Li}}+1,\, m_{\mathrm{F}}-1|S_{+i}I_{-j}|m_{\mathrm{Li}}m_{\mathrm{F}}\rangle|^2. \quad (3)$$

$g_{12}(\omega_{12})$ is a frequency distribution function which gives the probability that the dipole-dipole interaction can absorb the Zeeman energy left over. We can approximate this function by

$$g_{12}(\omega_{12})=\int_{-\infty}^{\infty} g_{\mathrm{Li}}(\omega)g_{\mathrm{F}}(\omega')\delta(\omega+\omega')P(\omega,\omega')d\omega d\omega'. \quad (4)$$

$g_{\mathrm{Li}}(\omega)$ and $g_{\mathrm{F}}(\omega')$ are the line shape functions observed in the usual absorption experiments, $\delta(\omega+\omega')$ is to account for conservation of energy, and $P(\omega,\omega')$ takes account of correlations that make it more difficult for the local fields to change by large amounts over short distances than over longer distances. Equation (4) can be approximated further by replacing $g_{\mathrm{Li}}(\omega)$ and $g_{\mathrm{F}}(\omega')$ by Gaussians with second moments given by Van Vleck[10] and setting $P=1$. The result is the Gaussian

$$g_{12}(\omega_{12})=\frac{1}{[2\pi(\Delta\omega_{\mathrm{Li}}^2+\Delta\omega_{\mathrm{F}}^2)]^{\frac{1}{2}}}\exp\left[\frac{1}{2}\frac{(\omega_{\mathrm{F}}-\omega_{\mathrm{Li}})^2}{\Delta\omega_{\mathrm{Li}}^2+\Delta\omega_{\mathrm{F}}^2}\right], \quad (5)$$

where $\omega_{12}=\omega_{\mathrm{F}}-\omega_{\mathrm{Li}}$.

In principle $g_{12}(\omega_{12})$ can be calculated exactly by a moment method. However the length of such a calculation limits us to just the second moment

$$(\Delta\omega)_{12}^2=\frac{1}{\hbar^2}\frac{\mathrm{Tr}|\mathcal{H}_1B'-B'\mathcal{H}_1|^2}{\mathrm{Tr}|B'|^2}. \quad (6)$$

A better approximation than Eq. (5) is to assume $g_{12}(\omega_{12})$ is a Gaussian with second moment given by

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[11] Leonard I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, New York, 1949), first edition, Chap. VIII.

Eq. (6) since it takes into account $P\neq 1$. Neglecting correlations would say the dipole-dipole interaction can absorb more energy than it really is able to, predicting cross relaxation at too high fields.

Neglecting lattice sums like

$$\sum_{i,j,k} A_{ij}'A_{kj}'A_{ik}^2,$$

compared with terms like

$$\sum_{i,j,k} (A_{ij}')^2A_{ik}^2,$$

Eq. (6) can be evaluated, for the (111) direction, giving $(1/2\pi)[(\Delta\omega)_{12}{}^2]^{\frac{1}{2}}\approx 11.8$ kc/sec compared to 15 kc/sec by the overlap integral of Eq. (5). Correlations make the distribution function narrower by a factor of 0.8. Putting numerical values into Eqs. (3) and (5), the cross-relaxation time $T_{21}$ can be obtained by a method to be explained later; the conclusion is $g_{12}(\omega_{12})$ is peaked so sharply about $\omega_{12}=0$, even when correlations are neglected, that above 40 gauss cross-relaxation times are larger than one minute.

A more likely mechanism for exchange of energy is if two Li's flip opposite to one F spin, the Zeeman energy left over in this process is less than $\frac{1}{3}$ the value for the simpler process, the exponent in Eq. (5) is reduced by a factor of 10, and the resulting increase in $g_{12}(\omega_{12})$ more than compensates for the reduction in the matrix element accompanying the necessarily higher order perturbation. Following conventional time-dependent perturbation theory, for initial state $|0\rangle$ the probability amplitude for final state $|\beta\rangle$ in which two Li's have flipped up and one F down is made up of a sum of terms like

$$b_\beta(t)_{ij:kl}=-\frac{1}{\hbar^2}\sum_\alpha B_{ij}'C_{kl}\times\left(\frac{\langle\beta|S_{+i}I_{-j}|\alpha\rangle\langle\alpha|S_{+k}S_{zl}+S_{+l}S_{zk}|0\rangle}{\omega(C_{kl})_{\alpha:0}}+\frac{\langle\beta|S_{+k}S_{zl}+S_{+l}S_{zk}|\alpha\rangle\langle\alpha|S_{+i}I_{-j}|0\rangle}{\omega(B_{ij}')_{\alpha:0}}\right)\times\frac{\exp(i\omega_{\beta:0}t)-1}{\omega_{\beta:0}}, \tag{7}$$

where $\hbar\omega(C_{kl})_{\alpha:0}$ is the energy difference between the states $|\alpha\rangle$ and $|0\rangle$ that are connected by $C_{kl}(S_{+k}S_{zl}+S_{zk}S_{+l})$, similarly for $\hbar\omega(B_{ij}')_{\alpha:0}$. The most naive approach would be to take the absolute value of the square of a sum of terms given by Eq. (7) and similar equations for other pairs of operators, integrate over a frequency distribution and obtain the transition probability. This can't be correct since it would mean the three spins which flip do not have to be physically near one another. In Eq. (7), spin "$i$" must be near spin "$j$" but "$k$" can be anywhere, the resultant transition probability would be too large by a factor $N$, equal to the number of spins in the crystal.

Since there can only be transitions between states that conserve energy we must consider only those terms in Eq. (7) for which $\omega_{\beta:0}\approx 0$, that is, only those states for which

$$\begin{aligned}\omega(C_{kl})_{\alpha:0}&\approx-\omega(B_{ij}')_{\beta:\alpha},\\ \omega(C_{kl})_{\beta:\alpha}&\approx-\omega(B_{ij}')_{\alpha:0}.\end{aligned}\tag{8}$$

Neglecting the small difference between $\omega(C_{kl})_{\alpha:0}$ and $\omega(C_{kl})_{\beta:\alpha}$ and similarly for $\omega(B_{ij}')_{\alpha:0}$ and $\omega(B_{ij}')_{\beta:\alpha}$, and taking a suitable average, the first approximation to these terms is

$$b_\beta(t)_{ij:kl}=\frac{-1}{\hbar^2}\frac{B_{ij}'C_{kl}}{2}\left(\frac{1}{\omega_{\mathrm{Li}}}+\frac{1}{\omega_{\mathrm{F}}-\omega_{\mathrm{Li}}}\right)\times\{\langle\beta|S_{+i}I_{-j}(S_{+k}S_{zl}+S_{+l}S_{zk})-(S_{+k}S_{zl}+S_{+l}S_{zk})S_{+i}I_{-j}|0\rangle\}\times\frac{\exp(i\omega_{\beta:0}t)-1}{\omega_{\beta:0}}. \tag{9}$$

This probability amplitude is significant only when the three spins which flip are near one another. Taking into account all necessary operators of the form of Eq. (9), the probability per unit time of a transition from $|0\rangle$ to $|\beta\rangle$ is

$$W_{0\rightarrow\beta}=\frac{2\pi}{\hbar^2}g_{12}(\omega_{12})|\langle\beta|\mathcal{H}_{12}|0\rangle|^2, \tag{10}$$

where

$$\begin{aligned}\langle\beta|\mathcal{H}_{12}|0\rangle=&\frac{1}{2\hbar}\left(\frac{1}{2\omega_{\mathrm{Li}}}+\frac{1}{\omega_{\mathrm{F}}}\right)\langle\beta|D'E-ED'|0\rangle\\&+\frac{1}{2\hbar}\left(\frac{1}{\omega_{\mathrm{F}}-\omega_{\mathrm{Li}}}+\frac{1}{\omega_{\mathrm{Li}}}\right)\langle\beta|B'C'-C'B'|0\rangle\\&+\frac{1}{2\hbar}\left(\frac{1}{\omega_{\mathrm{F}}-\omega_{\mathrm{Li}}}+\frac{1}{\omega_{\mathrm{Li}}}\right)\langle\beta|B'C-CB'|0\rangle,\end{aligned}$$

and neglecting correlations

$$g_{12}(\omega_{12})\approx\frac{1}{\{2\pi[2(\Delta\omega)_{\mathrm{Li}}{}^2+(\Delta\omega)_{\mathrm{F}}{}^2]\}^{\frac{1}{2}}}\times\exp\left(\frac{-(\omega_{\mathrm{F}}-2\omega_{\mathrm{Li}})^2}{2[2(\Delta\omega)_{\mathrm{Li}}{}^2+(\Delta\omega)_{\mathrm{F}}{}^2]}\right) \tag{11}$$

analogous to Eq. (5).

The second moment of $g_{12}(\omega_{12})$ is rigorously given by

$$\langle(\Delta\omega)_{12}{}^2\rangle=\frac{1}{\hbar^2}\frac{\mathrm{Tr}|\mathcal{H}_1\mathcal{H}_{12}-\mathcal{H}_{12}\mathcal{H}_1|^2}{\mathrm{Tr}|\mathcal{H}_{12}|^2}. \tag{12}$$

However, it is such a formidable task to just expand this out that no attempt was made to try and evaluate it. From the results of Eq. (6) for the two-spin process, we might expect correlations to cause $(\Delta\omega)_{12}^2$ to be anywhere from $\frac{1}{2}$ to $\frac{3}{4}$ of the second moment in Eq. (11).

When $\omega_{12}$ is equal to two or three times the second moment of Eq. (11), $g_{12}$ becomes very sensitive to the value of this moment. Since Van Vleck[10] has shown $(\Delta\omega)_{\mathrm{Li}}^2$ and $(\Delta\omega)_{\mathrm{F}}^2$ to be anisotropic, for a given magnetic field (i.e., constant $\omega_{12}$), $g_{12}$ and $T_{21}$ are also anisotropic. For large enough fields, small changes in linewidths caused by rotating the crystal can cause $g_{12}$ and thus $T_{21}$ to change by a couple of orders of magnitude, because the second moment of $g_{12}$ occurs in the exponent of a Gaussian.

### B. Rate Equations and Cross-Relaxation Time

Van Hove[12] and Philippot[13] have shown rigorously that for all but pathological situations rate equations can be written down for a spin system described by the Hamiltonian in Eq. (1). Our treatment of these equations is similar to Schumacher's[3] which is also equivalent to the somewhat different procedure followed in BSPA. Assume the rate of exchange of energy between the Li and F systems is much slower than the time necessary for a Boltzmann distribution to be established in each system separately, (i.e., $T_{21}\gg T_2$). We can then define an Li spin temperature $\theta$ and an F spin temperature $T$, where $\theta$ is not equal to $T$ in general.

Let $p$ be the density matrix for the Li spins and $P$ for the F spins. Since the two systems are separately in thermal equilibrium with themselves, $p$ and $P$ are both diagonal. Neglecting the dipole-dipole interaction we have $\langle E_{\mathrm{Li}}\rangle=\mathrm{Tr}\,p\mathcal{H}_0{}^{\mathrm{Li}}$, $\langle E_{\mathrm{F}}\rangle=\mathrm{Tr}\,P\mathcal{H}_0{}^{\mathrm{F}}$,

$$p_a=\frac{\langle a|\exp(-\mathcal{H}_0{}^{\mathrm{Li}}/k\theta)|a\rangle}{\mathrm{Tr}\exp(-\mathcal{H}_0{}^{\mathrm{Li}}/k\theta)},\qquad P_b=\frac{\langle b|\exp(-\mathcal{H}_0{}^{\mathrm{F}}/kT)|b\rangle}{\mathrm{Tr}\exp(-\mathcal{H}_0{}^{\mathrm{F}}/kT)}. \tag{13}$$

If $W_{a'b'\to ab}$ is the probability of a transition from a state $a'b'$ to $ab$, by the principle of detailed balance we have

$$\frac{W_{a'b'\to ab}}{W_{ab\to a'b'}}=\exp\left[\frac{E_{a'}{}^{\mathrm{Li}}-E_a{}^{\mathrm{Li}}+E_{b'}{}^{\mathrm{F}}-E_b{}^{\mathrm{F}}}{kT_S}\right],$$

where $T_S$ is the equilibrium spin temperature, where

$$\frac{d}{dt}\langle E_{\mathrm{Li}}\rangle=\mathrm{Tr}\,\mathcal{H}_0{}^{\mathrm{Li}}\dot{p}=\frac{\partial E_{\mathrm{Li}}}{\partial\theta}\frac{d\theta}{dt}, \tag{14}$$

and

$$\dot{p}_a=\sum_{a'b'b}p_{a'}P_{b'}W_{a'b'\to ab}-p_aP_bW_{ab\to a'b'}. \tag{15}$$

Combining Eqs. (13), (14), and (15) with similar ones for $\langle E_{\mathrm{F}}\rangle$ and $P_\beta$ we obtain

$$\frac{d}{dt}\left(\frac{1}{\theta}\right)=-\alpha\left(\frac{1}{\theta}-\frac{1}{T_S}\right)+\beta\left(\frac{1}{T}-\frac{1}{T_S}\right),\qquad \frac{d}{dt}\left(\frac{1}{T}\right)=-\bar{\alpha}\left(\frac{1}{T}-\frac{1}{T_S}\right)+\bar{\beta}\left(\frac{1}{\theta}-\frac{1}{T_S}\right), \tag{16}$$

where if the number of Li and F spins are each $N$

$$\alpha=\frac{6W}{NS(S+1)(2S+1)^N(2I+1)^N},$$

$$\beta=\frac{1}{2}\frac{\omega_{\mathrm{F}}}{\omega_{\mathrm{Li}}}\alpha,$$

$$\bar{\alpha}=\frac{1}{4}\frac{S(S+1)}{I(I+1)}\alpha,$$

$$\bar{\beta}=\frac{1}{2}\frac{S(S+1)}{I(I+1)}\frac{\omega_{\mathrm{Li}}}{\omega_{\mathrm{F}}}\alpha,$$

$$W=\sum_{ab,a'b'}W_{a'b'\to ab}.$$

Solving Eqs. (16), one of the time constants is infinite corresponding to an infinite $T_1$ for a rigid lattice, the other one is

$$1/T_{21}=\alpha+\bar{\alpha}. \tag{17}$$

From the transition probability given by Eq. (10) and Eqs. (16) and (17)

$$\begin{aligned}\frac{1}{T_{21}}=&\frac{2\pi g_{12}(\omega_{12})}{(\hbar H_0)^2N}[4I(I+1)+S(S+1)]\\ &\times\left\{\frac{4}{9}S(S+1)\left[\left(\frac{\gamma_{\mathrm{F}}+2\gamma_{\mathrm{Li}}}{2\gamma_{\mathrm{F}}\gamma_{\mathrm{Li}}}\right)^2\sum_{i,j,k}|E_{ij}D_{jk}'|^2\right.\right.\\ &+\left(\frac{1}{2}\frac{\gamma_{\mathrm{F}}}{\gamma_{\mathrm{Li}}(\gamma_{\mathrm{F}}-\gamma_{\mathrm{Li}})}\right)^2\sum_{i,j,k\,(i\neq j)}|B_{ij}'C_{jk}'|^2\\ &+\left(\frac{\gamma_{\mathrm{F}}}{\gamma_{\mathrm{Li}}(\gamma_{\mathrm{F}}-\gamma_{\mathrm{Li}})}\right)^2\sum_{i,j,k}(|B_{ik}'C_{ij}|^2\\ &\left.+B_{ik}'B_{jk}'|C_{ik}|^2)\right]+\frac{8}{15}[S(S+1)-\tfrac{3}{4}]\\ &\left.\times\left(\frac{\gamma_{\mathrm{F}}}{2\gamma_{\mathrm{Li}}(\gamma_{\mathrm{F}}-\gamma_{\mathrm{Li}})}\right)^2\sum_{i,k}|B_{ik}'C_{ik}'|^2\right\},\end{aligned} \tag{18}$$

where the last term comes from one Li flipping twice. Using $\gamma_{\mathrm{Li}}=2\pi\times1655$ (gauss sec)$^{-1}$, $\gamma_{\mathrm{F}}=2\pi\times4007$ (gauss sec)$^{-1}$ and carrying out the lattice sums to the

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[12] L. Van Hove, Physica **21**, 517 (1955); Physica **23**, 441 (1957).

[13] Jean Philippot, thesis, Université Libre de Bruxelles, 1959 (unpublished).

122nd nearest neighbor, the results in Table I are obtained. The last column is that value of $H_0$ for which the overlap integral approximation [Eq. (11)] predicts $T_{21}=1$ second.

To take the finite spin-lattice relaxation times into account we modify Eqs. (16) as follows,[3]

$$\frac{d}{dt}\left(\frac{1}{\theta}\right)=-\alpha\left(\frac{1}{\theta}-\frac{1}{T_S}\right)+\beta\left(\frac{1}{T}-\frac{1}{T_S}\right)-\frac{1}{T_{1(\mathrm{Li})}}\left(\frac{1}{\theta}-\frac{1}{T_l}\right),$$

$$\frac{d}{dt}\left(\frac{1}{T}\right)=-\bar{\alpha}\left(\frac{1}{T}-\frac{1}{T_S}\right)+\bar{\beta}\left(\frac{1}{\theta}-\frac{1}{T_S}\right)-\frac{1}{T_{1(\mathrm{F})}}\left(\frac{1}{T}-\frac{1}{T_l}\right), \tag{19}$$

where $T_l$ is the lattice temperature, $T_{1(\mathrm{Li})}$ and $T_{1(\mathrm{F})}$ are the Li and F spin-lattice relaxation times, respectively. The two time constants associated with Eqs. (19) are $\lambda_+$ and $\lambda_-$; with the aid of Eq. (17) we define

$$\frac{1}{T_{10}}=\lambda_-=\frac{1}{2}\left\{\frac{1}{T_{21}}+\frac{1}{T_{1(\mathrm{F})}}+\frac{1}{T_{1(\mathrm{Li})}}-\frac{1}{T_{21}}\left[1+\frac{2T_{21}}{9}\left(\frac{1}{T_{1(\mathrm{F})}}-\frac{1}{T_{1(\mathrm{Li})}}\right)+T_{21}^2\left(\frac{1}{T_{1(\mathrm{F})}}-\frac{1}{T_{1(\mathrm{Li})}}\right)^2\right]^{\frac{1}{2}}\right\}, \tag{20}$$

$$\frac{1}{\tau}=\lambda_+-\lambda_-=\frac{1}{T_{21}}\left[1+\frac{2T_{21}}{9}\left(\frac{1}{T_{1(\mathrm{F})}}-\frac{1}{T_{1(\mathrm{Li})}}\right)+T_{21}^2\left(\frac{1}{T_{1(\mathrm{F})}}-\frac{1}{T_{1(\mathrm{Li})}}\right)^2\right]^{\frac{1}{2}}.$$

In the limit of $T_{21}\ll T_1$, $\tau$ is equal to $T_{21}$, while if $T_{21}$ is infinite $1/\lambda_-=T_{1(\mathrm{Li})}$ and $1/\lambda_+=T_{1(\mathrm{F})}$.

The Li (or F) signal as a function of the time $t$ at $H_0$ is

$$S=e^{-t/T_{10}}[A+B(1-e^{-t/\tau})]+C, \tag{21}$$

where $A$, $B$, and $C$ are determined by the initial conditions, lattice temperature $T_l$, and $H_0$.

TABLE I. Numerical results of calculations on cross relaxation in LiF single crystals.

| Crystal orientation | $(H_0^2/T_{21}g_{12})$ (gauss/sec)$^2$ | $H_0(T_{21}=1$ sec) (gauss) |
|---|---|---|
| 100 | $1.34\times10^{11}$ | 104 |
| 110 | $3.88\times10^{11}$ | 88 |
| 111 | $1.15\times10^{11}$ | 67 |

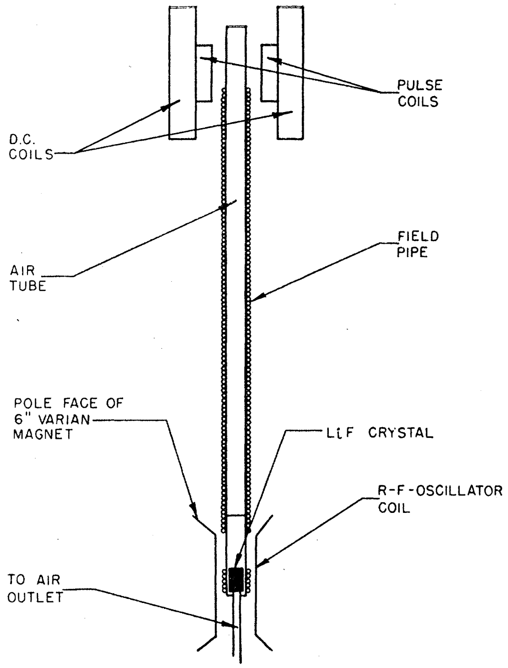

FIG. 1. Experimental arrangement for moving the sample from 4600 gauss to $H_0$ in which cross relaxation takes place.

## III. EXPERIMENT

$T_{21}$ is measured by the same method Abragam and Proctor[1] first used. An LiF crystal is allowed to come into equilibrium with the lattice in a field of 4600 gauss, the Li spins are then saturated and the crystal is quickly moved to a field $H_0$ of the order of 50 gauss, where cross relaxation takes place. The sample is kept there for a measured length of time and then brought back to 4600 gauss where the Li magnetization is then measured.

Since this is all done fast compared to the spin-lattice relaxation time there can only be nonzero Li magnetization via cross relaxation. The time at the low field is varied and the data fit to Eq. (21). This fit can be made even though the time necessary to move the sample is not really negligible compared to $T_1$; $A$, $B$, and $C$ are functions of various times in the measurement process but care can be taken to make each measurement in exactly the same way so in any one plot of magnetization *vs* time they really are constants. Spin-lattice relaxation times in pure LiF crystals are a couple of minutes long so it is not difficult to do things fast compared with $T_1$.

This experiment is different from Abragam and Proctor's in the way we move the sample from 4600 gauss to $H_0$, the apparatus shown in Fig. 1 was constructed for this purpose. The sample is shown in the rf coil used to both saturate and detect the Li magnetization at the bottom of the air tube. The crystal is glued to a plastic piece that has a square cross section, the inside of the air tube is also square which keeps the sample from rotating. The field pipe is a solenoid 80 cm long, and when activated it supplies 120 gauss along the entire length of the air pipe. At the top of the field pipe are two Helmholtz coils that can rotate about the axis of the pipe, the dc coils supply the field $H_0$, the pulse coils supply about 80 gauss parallel to $H_0$. After the Li magnetization is saturated, the field pipe is turned on and the crystal is shot up and kept at the Helmholtz coils by compressed air. When the crystal is at the top the field pipe is turned off. Since the 4 seconds it takes to reach the top of the pipe is much smaller than $T_1$ or $T_{21}$ and since the mechanical motion is slow compared to $T_2$ this is a reversible adiabatic demagnetization.[1,3,14–17] The crystal is now in a field of $H_0+80$ gauss large enough to make $T_{21}$ very long, the 80 gauss are turned off for a measured length of time and then on again. During the time it is off cross relaxation takes place at a rate determined by $H_0$ and the orientation of the Helmholtz coils, when the 80 gauss come on again cross relaxation stops and the Li magnetization is frozen in. The field pipe is turned on again, the air turned off and the sample falls into the rf coil where the Li magnetizaton is measured. The pulsed field is turned off and on by a current-regulated power supply triggered by a one-shot multivibrator. The pulse width can be varied from 0.003 second to 24 seconds; longer times can be done manually. Transitients obvseved by a pickup coil and a Tektronix 535 oscilloscope die out in 1 millisecond, and pulse widths are measured this way to better than 3%.

The dc Helmholtz coils have been calibrated with dpph at 70 Mc/sec to better than 1%, they are air cored so the field is strictly proportional to current; current was measured with the same Weston dc ammeter during the experiment and calibration. Homogeneity was better than 0.5% over the sample volume. Field orientation was measured to better than 0.2° by means of marks every degree on the outer circumference of the rotating table holding the coils, it was 50 cm in diameter.

The spins were observed with a Pound-Watkins[18] type spectrometer in which the oscillator section was replaced by one given by Mays, Moore, and Shulman[19] and an extra stage of rf gain was added to improve the *AVC* control at low levels. The oscillation level was adjusted so the Li signal would saturate in approximately 5 seconds, and the frequency was swept so that it took about 10 seconds to go through the line. The output of the spectrometer was fed into a phase sensitive lock-in detector[18] that had a time constant of 0.5 second. The output of the lock-in was recorded on an Esterline Angus recorder. Keeping all other parameters constant the recorded signal is proportional to the magnetization immediately before the line is swept through. Since proportionality depends on the system being linear an experiment was done to prove linearity. The Li signal was saturated, and, without moving the sample from the field, we waited a measured length of time before sweeping back and observing the line. When the resultant signal was plotted as a function of the time waited, it was of the form $(1-e^{-t/T_1})$. The excellent fit to an exponential is proof the system really is linear. This is the way we measured $T_1$ in high fields.

In order to fit our data to Eq. (21) we had to make sure each point in a signal *vs* time plot was measured is exactly by the way. This was done in the following manner. The line was saturated by sweeping through it three times. A radio receiver was tuned to a frequency just off one side of the resonance line, when audio beats were heard in the receiver after the third pass through the line, a stop watch was started. At 5 seconds the sweep motor was shut off and simultaneously the sample was shot up the tube, where the field pipe was already on. This time was never in error by more than 0.5 second. It always took 4 seconds for the sample to reach the top of the tube, at which time the field pipe was turned off and the pulse triggered; this was done in less than one second. The field pulse was observed on an oscilloscope so that within 0.5 second after the 80 gauss came on again, the field pipe was turned on and the sample was falling back to the rf coil. It took 4 seconds to reach the bottom. Within 0.5 second of reaching bottom the sweep motor was turned on again and the signal was recorded 9 seconds later. Excluding the time during which cross relaxation took place, the entire process lasted 23±2 seconds.

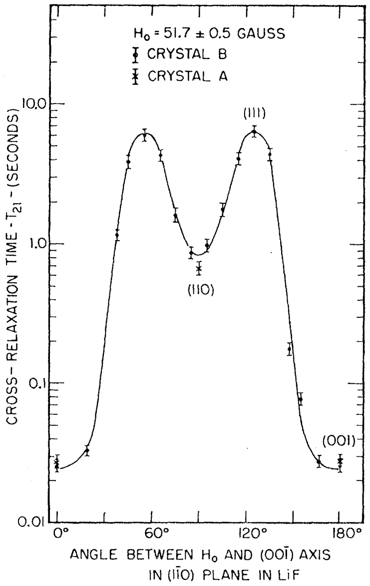

FIG. 2. Cross-relaxation time $T_{21}$ *vs* angle in the $(1\bar{1}0)$ plane of LiF, crystal *B*, at 51.7 gauss. The cross marks in the [110] and [001] directions are taken from crystal *A*.

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[14] R. V. Pound and N. F. Ramsey, Phys. Rev. **81**, 278 (1951).

[15] L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

[16] A. Sachs and E. Turner, thesis, Harvard University, 1949 (unpublished).

[17] A. G. Anderson, Phys. Rev. **115**, 863 (1959).

[18] George D. Watkins, thesis, Harvard University, 1952 (unpublished).

[19] Mays, Moore, and Shulman, Rev. Sci. Instr. **29**, 300 (1958).

Since measurements were reproduceable to within the error expected from the noise of the detection system, i.e., less than 5%, we are confident that we were able to keep $A$, $B$, and $C$ constant.

Two crystals were used; both were cut in the form of right circular cylinders, diameter 1 cm and length 2 cm. In crystal $A$ the axis of symmetry was the [100], in crystal $B$ it was the [110] axis. Crystal $A$ was considerably purer than crystal $B$; this was reflected in the spin-lattice relaxation times,[20] in 4600 gauss $T_1(\text{Li})$ was 8 minutes in crystal $A$ but only 4 minutes in crystal $B$.

## IV. RESULTS

Figure 2 shows the anisotropic behavior of $T_{21}$ predicted in a previous communication,[8] except for the three points taken from crystal $A$, it was taken in the $(1\bar{1}0)$ plane of crystal $B$. The excellent agreement between two crystals with very different spin-lattice relaxation times is evidence that impurities do not play any role in cross relaxation.

The qualitative agreement between the curve in Fig. 2 and the overlap integral approximation is excellent. Cross-relaxation times are longest when the magnetic field is in the [111] direction, this is also the direction in which the absorption lines are narrowest, making $g_{12}$ [Eq. (11)] smallest. $T_{21}$ is shortest in the [100] direction, where the absorption lines are broadest. The similarity between the shape of Fig. 2 in this paper and Fig. 2 in reference 10 is a very clear demonstration of the dependence of $T_{21}$ on linewidths. The anisotropy is so very large, a factor of 500 in 54°, because the probability that energy can be conserved changes rather drastically as the crystal is rotated.

The field dependence of $T_{21}$ is shown in Fig. 3 for three orientations; the [111] direction was taken on crystal $B$, the other two curves on crystal $A$. The fields at which $T_{21}=1$ second are 0.6 to 0.7 times the fields predicted by the overlap integral approximation in Table I. Since this approximation ignored correlations, we expect it to predict too large fields. For the [111] direction the exact calculation of the second moment for the two spin process [Eq. (6)] was 0.8 times the value from the overlap integral for that process. Since the cross-relaxation process we are studying is more complicated than the two-spin model it is to be expected that correlations have a larger effect and 60 to 70% is a reasonable amount.

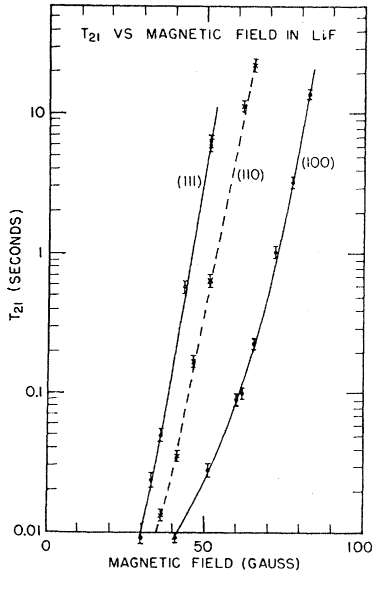

FIG. 3. Cross-relaxation time $T_{21}$ *vs* $H_0$ for three crystal orientations. The [111] direction was taken on crystal $B$, the [110] and [100] were from crystal $A$.

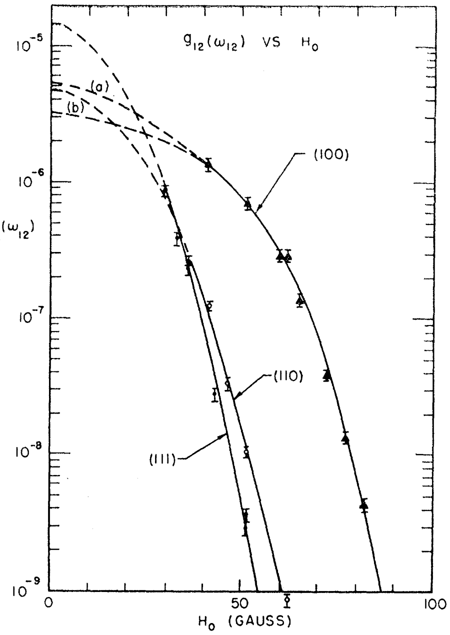

FIG. 4. $g_{12}(\omega_{12})$ *vs* $H_0$, $\omega_{12}=2\pi 697 H_0$. The curve for the [110] direction is $g_{12}=0.49\times10^{-5}\exp[-\nu_{12}^2/2(10.3\text{ kc/sec})^2]$, and for the [111] direction $g_{12}=1.4\times10^{-5}\exp[-\nu_{12}^2/2(8.8\text{ kc/sec})^2]$.

These results are also consistent with Abragam and Proctor's measurement of $T_{21}=6$ seconds at 75±10 gauss. They paid no attention to orientation so we might assume their measurement yielded the shortest cross-relaxation time for a given field, that should be for the [100] direction where $T_{21}=2$ seconds at 75 gauss and 6 seconds at 79 gauss.

From Fig. 3 and Table I we calculated $g_{12}(\omega_{12})$ as a function of field ($\omega_{12}=2\pi 697 H_0$), and the results are plotted in Fig. 4. The data for both the [111] and [110] could be fit to Gaussians throughout the three decades we were able to measure. However, the results for the [100] direction could not possibly be described by one Gaussian. The Gaussians that describe the tails of $g_{12}(\omega_{12})$ are also good approximations near the center, $\omega_{12}=0$. Since $g_{12}(\omega_{12})$ is normalized to unity

$$\int_{-\infty}^{\infty} g_{12}(\omega_{12})d\omega_{12}=1.$$

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[20] N. Bloembergen, Physica **15**, 386 (1949).

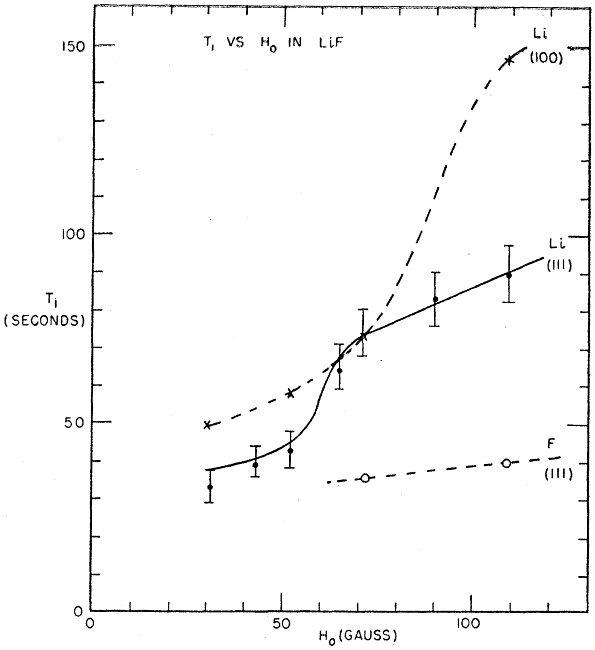

FIG. 5. Spin-lattice relaxation times *vs* $H_0$ in LiF. For the [100] direction $T_1$ is given for Li, for the [111] direction $T_1$ is given for both Li and F, the solid curve is the theoretical function as explained in the text.

Assuming these functions are symmetric about the origin the results are 1.9 for the [111] direction and 0.8 for the [110] direction. In view of the fact that the closest we can get to the center of the line is 0.1 $g_{12}(0)$, the agreement is remarkable. There is every reason to believe the absorption lines have the same qualitative shape as $g_{12}(\omega_{12})$ and thus are also Gaussian in the [111] and [110] direction. In the [100] direction we could not describe $g_{12}(\omega_{12})$ by a Gaussian, however we did make the two extrapolations (a) and (b) that seem to be the limits of reasonable curves; assuming symmetry about the origin the integral from $-\infty$ to $+\infty$ is 1.0 for curve (b) and 1.4 for curve (a), agreement is again excellent.

Curve (b) is very flat and broad near the center and the extrapolation may seem unrealistic. Numerical integration for curve (b) gives

$$[\langle\Delta\omega_{12}^4\rangle]^{\frac{1}{4}}/[\langle\Delta\omega_{12}^2\rangle]^{\frac{1}{2}}=1.26.$$

Van Vleck[10] calculates this same ratio for a simple cubic lattice of spins $\frac{1}{2}$ to be 1.25 in the (100) direction indicating that curve (b) is reasonable.

Watkins[18] observed that in large magnetic fields the spin-lattice relaxation time of Li in LiF is anisotropic.[21] Figure 5 shows $T_1$ for Li as a function of field for the [100] and [111] orientations of crystal $B$, and for the [111] direction the $T_1$ of F is also shown. At 109 gauss the anisotropy is the same as Watkins observed. However, as the field is lowered, it changes considerably, and at 71 gauss $T_1$ is the same for both directions. At this field $T_{21}$ is less than 1 second in the [100] direction and since the F spin-lattice relaxation is more rapid than the Li, the easiest way for the Li's to come into equilibrium with the lattice is by first coming into equilibrium with the F's which then come into equilibrium with the lattice, the apparent $T_1$ of Li is lowered. In the [111] direction however, $T_{21}$ is more than 100 seconds at 71 gauss and this drop has not yet begun; the slow decrease of the Li $T_1$ above 70 gauss is not associated with cross relaxation.[22]

Assuming in the absence of $T_{21}$ the $T_1$'s in the [111] direction would continue to decrease along the straight lines they follow above 70 gauss, from Fig. 3 and Eq. (20) we can calculate $T_{10}$ *vs* $H_0$. The solid curve for Li in the [111] direction is the result. The theoretical curve is an excellent fit to the measured values of $T_{10}$.

## V. CONCLUSIONS

1. The theory of BSPA is correct. Cross-relaxation times can be predicted if one takes into account all the necessary interactions.[23]

2. The tails of line shapes for nuclear magnetic absorption can be inferred from cross-relaxation measurements. For LiF in the [111] and [110] directions they are very well approximated by Gaussians, in the [100] direction a Gaussian is a poor approximation.

3. The validity of rate equations to describe cross relaxation is established. Cross relaxation is an irreversible process in which two-spin systems come into thermal equilibrium with one another.

## ACKNOWLEDGMENTS

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[21] We are indebted to Dr. A. Redfield for suggesting the investigation of $T_1$ in low field.

[22] E. G. Wikner and E. L. Hahn, Bull. Am. Phys. Soc. 3, 325 (1958).

[23] Quadrupole effects must be taken into account in order to explain the results of reference 3.