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Anisotropic nuclear spin relaxation in single-crystal xenon

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We extend the theory of longitudinal spin relaxation of ^{129}Xe nuclei in frozen xenon to the case of single-crystal samples, where the relaxation rate depends on the direction of the applied magnetic field with respect to the crystalline axes. For sufficiently large magnetic fields, the relaxation is dominated by spin-flip Raman scattering of lattice phonons. Two closely related interactions couple the lattice phonons to the spins of ^{129}Xe nuclei: the nuclear spin-rotation interaction between nearest-neighbor atoms, which leads to an isotropic, field-independent relaxation rate, and the paramagnetic antishielding of the externally applied field at the site of ^{129}Xe nuclei by the electrons of neighboring Xe atoms. The latter interaction, also known as the chemical shift anisotropy (CSA) interaction, leads to an anisotropic relaxation rate proportional to the square of the applied field. This mechanism dominates spin relaxation at fields of the order of the Debye field $B_D = k_B T_D / \mu_B = 82$ T.

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I. INTRODUCTION

The nuclear spin relaxation of ^{129}Xe in cold xenon crystals is of considerable current interest because the cryogenic condensation of gaseous xenon is used to accumulate large quantities of hyperpolarized ^{129}Xe for medical imaging and other applications.[1,2] There is good experimental and theoretical evidence[3,4] that nuclear spin relaxation in solid xenon — at temperatures between 20 and 100 K, and at magnetic fields above 0.1 T and less than a few T — is dominated by phonon-induced fluctuations of the spin-rotation interaction

$$v = \frac{c_K}{\hbar} \mathbf{K} \cdot \mathfrak{I} \cdot \boldsymbol{\omega} = c_K \mathbf{K} \cdot \mathbf{N}. \tag{1.1}$$

Here $\mathbf{K}$ is the nuclear spin of a ^{129}Xe atom, and the angular momentum $\mathbf{N}$ of the pair of atoms is related to the angular velocity $\boldsymbol{\omega}$ of their relative rotation about each other by

$$\hbar \mathbf{N} = \mathfrak{I} \cdot \boldsymbol{\omega}. \tag{1.2}$$

The inertial tensor $\mathfrak{I}$ of the pair is

$$\mathfrak{I} = \frac{M}{2} (R^2 \mathbf{1} - \mathbf{R}\mathbf{R}). \tag{1.3}$$

The mass of a xenon atom is M, and $\mathbf{R}$ is the internuclear displacement of the pair. As indicated in Fig. 1, the unit vectors $\mathbf{x}_1$, $\mathbf{x}_2$, and $\mathbf{x}_3$ point along the fourfold symmetry axes of the crystal. We use the notation of Ramsey and co-workers[5,6] for the coupling coefficient $c_K = c_K(R)$, which will depend on the internuclear separation R of the pair of atoms.

For externally applied magnetic fields $\mathbf{B}_0$ exceeding a few T, there will be a substantial contribution to the relaxation rate from phonon-induced fluctuations of the paramagnetic antishielding interaction

$$v' = \frac{c_K}{\hbar} \mathbf{K} \cdot \mathfrak{I} \cdot \boldsymbol{\omega}_0. \tag{1.4}$$

Here the Larmor frequency of an electron of mass m is $\boldsymbol{\omega}_0 = e\mathbf{B}_0/2mc$, and the coupling coefficient c_K is the same as that in Eq. (1.1). The chemical shifts produced by the interactions v and v', and their relationship to the spin-relaxation rates, were discussed for the case of linear molecules in a liquid by Spiess *et al.*[7]

Fitzgerald *et al.*[4] (henceforth referred to as Fitzgerald) showed how the interactions v and v' of Eqs. (1.1) and (1.4) cause spin relaxation by the Raman scattering of phonons. The relaxation due to emission or absorption of single phonons was shown[4] to be completely negligible compared to Raman scattering. Fitzgerald[4] considered polycrystalline samples of xenon, and assumed that the observed relaxation rates could be obtained by averaging over all possible orientations of the crystallites. This procedure can be justified for samples with crystallites much smaller than the spin diffusion length during the longitudinal relaxation time T_1. As we shall show in this paper, the relaxation rate due to fluctuations in the paramagnetic antishielding depends strongly on the direction of the magnetic field with respect to the crystalline axes. For coarse-grained polycrystalline samples, where the size of the individual crystallites is much larger than the spin-diffusion length, a nonexponential decay can be expected at high magnetic fields, as discussed by Wolf[8] and by Barton and Sholl[9] for the angular dependence of the relaxation induced by the magnetic dipole-dipole interaction and the translational diffusion of nuclear spins in single crystals.

In this paper we extend the theory of Fitzgerald[4] to the case of single-crystal xenon. The simple, face-centered-cubic structure of the xenon crystal allows us to use group theory to simplify the calculational details, which can be found in the subsequent sections of this paper. Here we summarize the results.

The predicted longitudinal spin-relaxation rate $1/T_1^S$, due to fluctuations in the spin-rotation interaction of Eq. (1.1), is the same for single-crystal samples of xenon as for polycrystalline samples, and it is therefore given by Eq. (1.5) of Fitzgerald.[4]

The relaxation rate $1/T_1^P$ due to fluctuations in the para-

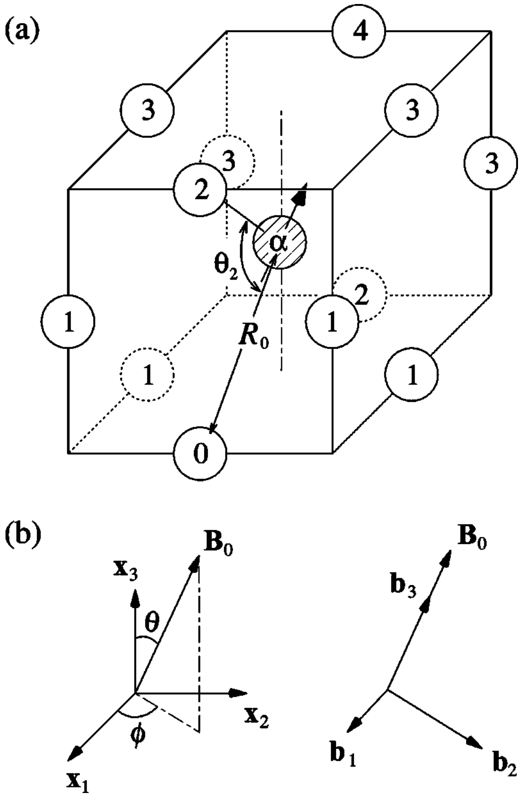

FIG. 1. (a) The 12 nearest neighbors of a ^{129}Xe atom α, separated from it by a distance R_0. The 144 ordered pairs of the nearest neighbor atoms can be partitioned into five sets Λ_m, with $m=0$, 1, 2, 3, and 4. If we label one of the neighbor atoms as "0," then pairs of atoms labeled (0,0), (0,1), . . . ,(0,4) will be representatives of the sets Λ_m for $m=0,1,\ldots,4$, respectively. For all pairs in a given set Λ_m, the two atoms are separated by the same distance, $R_0\sqrt{m}$, and subtend the same angle θ_m at the central atom α. Angle θ_2 is shown for pair (0,2). (b) Orientation of the externally applied magnetic field $\mathbf{B}_0$ is shown with respect to the crystal basis vectors $\mathbf{x}_1$, $\mathbf{x}_2$, and $\mathbf{x}_3$ (left), and the basis vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$, described in the text (right).

magnetic antishielding interaction of Eq. (1.4) differs from that in polycrystalline samples. The single-crystal rate is given by

$$\frac{1}{T_1^P}=\frac{9\pi c_{K0}^2 T^{*2} B^{*2}[\eta^P+\kappa^P Y]}{4\hbar^2\omega_D}. \tag{1.5}$$

Here $c_{K0}=c_K(R_0)$ is the spin-rotation coupling coefficient at the equilibrium separation R_0 of adjacent xenon atoms in the crystal. The Debye frequency is $\omega_D=k_BT_D/\hbar$, where $k_B=1.38\times10^{-16}$ erg K^{-1} is the Boltzmann constant. The Debye temperature of the xenon crystal is $T_D=55$ K, and $T^*=T/T_D$ is the relative temperature. The relative magnetic field is defined as $B^*=B_0/B_D$, where the Debye field for solid xenon is $B_D=k_BT_D/\mu_B=82$ T. The Bohr magneton is $\mu_B=0.9272\times10^{-20}$ erg G^{-1}.

The dependence on the field direction [see Fig. 1(b)],

$$\mathbf{b}_3=\frac{\mathbf{B}_0}{B_0}=\mathbf{x}_1\sin\theta\cos\phi+\mathbf{x}_2\sin\theta\sin\phi+\mathbf{x}_3\cos\theta, \tag{1.6}$$

is given by the function

$$\begin{aligned}Y=Y(\theta,\phi)&=\sum_{i=1}^{3}(\mathbf{x}_i\cdot\mathbf{b}_3)^4-\frac{3}{5}\\&=\sin^4\theta(\cos^4\phi+\sin^4\phi)+\cos^4\theta-\frac{3}{5}.\end{aligned} \tag{1.7}$$

Note that $\int_0^\pi\sin\theta d\theta\int_0^{2\pi}d\phi Y(\theta,\phi)=0$. In 1963, Eisenstadt and Redfield[10] pointed out that the orientation dependence of relaxation rates in cubic crystals will always have the form of Eq. (1.7).

The isotropic efficiency $\eta^P=\eta^P(\epsilon_0,T^*)$ of the paramagnetic antishielding relaxation is

$$\eta^P(\epsilon_0,T^*)=\sum_{p=1}^{5}\sum_{q=1}^{5}\epsilon_0^{5-p}E_{pq}^P D'_{q-1}(T^*), \tag{1.8}$$

where the coefficients E_{pq}^P are elements of the matrix

$$E^P=\frac{1}{20}\begin{bmatrix}8&-1&0&-1&8\\64&58&-16&58&64\\272&395&88&395&272\\288&1152&576&1152&288\\240&960&480&960&240\end{bmatrix}, \tag{1.9}$$

and the phonon freeze-out functions, defined by Eq. (2.48) of Fitzgerald,[4] are

$$D'_m=\frac{1}{T^{*2}}\int_0^1 du u^2\frac{e^{u/T^*}}{(e^{u/T^*}-1)^2}J_m^2(u). \tag{1.10}$$

Here the integration parameter $u=k/k_D$ is the ratio of the phonon momentum $\hbar k$ to the Debye momentum $\hbar k_D=\hbar\omega_D/c_s$, where we assume a common speed of sound c_s for the longitudinal and transverse modes. The functions $D'_m(T^*)$ are spectral averages of the phonon response functions $J_m(u)$, given by Eq. (2.36) of Fitzgerald[4] as

$$J_m(u)=1+j_0(u\phi_D\sqrt{m})-2j_0(u\phi_D), \tag{1.11}$$

where $j_0(x)=x^{-1}\sin x$ denotes a spherical Bessel function of zeroth order (or a "sinc" function). The Debye phase is $\phi_D=(6\pi^2\sqrt{2})^{1/3}$. For an emitted or absorbed phonon of relative momentum u, the function $J_m(u)$ defines the contribution to the relaxation from members β and δ of the nearest-neighbor pairs in the set Λ_m, for which $\cos\theta_m=1-(m/2)$. The set index can take on the values $m=0$, 1, 2, 3, and 4.

The anisotropic efficiency $\kappa^P=\kappa^P(\epsilon_0,T^*)$ is

$$\kappa^P(\epsilon_0,T^*)=\sum_{p=1}^{4}\sum_{q=1}^{5}\epsilon_0^{5-p}K_{pq}^P D'_{q-1}(T^*), \tag{1.12}$$

where the coefficients K_{pq}^P are elements of the matrix

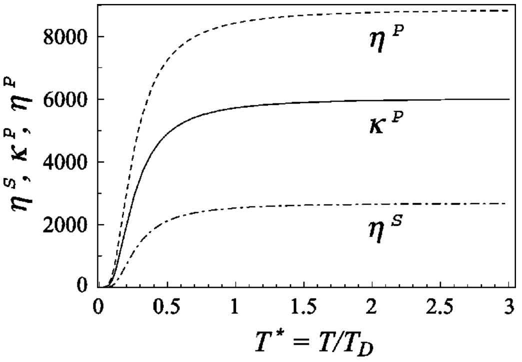

FIG. 2. The efficiency function $\kappa^P(\epsilon_0, T^*)$ (solid line) of Eq. (1.5) parametrizes the anisotropic part of ^{129}Xe spin relaxation due to spin-flip Raman scattering of phonons through the paramagnetic antishielding interaction [Eq. (1.4)]. For comparison, the efficiency functions $\eta^P(\epsilon_0, T^*)$ (dashed line) and $\eta^S(\epsilon_0, T^*)$ (dash-dotted line) are also shown—they parametrize the orientation-averaged relaxation due to interaction (1.4) and the field-independent relaxation due to spin-flip Raman scattering of phonons through the spin-rotation interaction (1.1), respectively. $T^* = T/T_D$ is the ratio of the crystal temperature T to the Debye temperature $T_D = 55$ K. For all three functions, an estimate (Ref. 4) of $\epsilon_0 = -11.8$ was used. The functions η^P, κ^P, and η^S approach the constants 8874.1, 6033.1, and 2686.8, respectively, for $T^* \gg 1$.

$$K^P = \frac{1}{8}\begin{bmatrix} 2 & 1 & 0 & 1 & 2 \\ 16 & 22 & -24 & 22 & 16 \\ 28 & 85 & -188 & 85 & 28 \\ -8 & -32 & -16 & -32 & -8 \end{bmatrix}. \qquad (1.13)$$

The efficiencies η^P and κ^P, given by Eqs. (1.8) and (1.12), parametrize relaxation (1.5) caused by fluctuations in the paramagnetic antishielding interaction (1.4) in a similar way that the efficiency η^S, given by Eq. (2.42) of Fitzgerald,[4] parametrizes relaxation caused by the spin-rotation interation [Eq. (1.1)]. All three efficiencies are plotted as a function of relative temperature $T^* = T/T_D$ in Fig. 2. The efficiencies are nearly independent of temperature above the Debye temperature ($T^* > 1$), but they diminish rapidly below the Debye temperature ($T^* < 1$), because the mean number of phonons n_ω in modes of frequency $\omega \sim \omega_D$ begins to freeze out, and is no longer well approximated by $n_\omega = kT/\hbar\omega$.

Let $\mathcal{R}$ be the ratio of the total relaxation rate, $1/T_1^S + 1/T_1^P$, to the field-independent rate $1/T_1^S$. Then we have

$$\mathcal{R} = \left[\frac{1}{T_1^S} + \frac{1}{T_1^P}\right] T_1^S = 1 + \left(\frac{\eta^P}{\eta^S} + \frac{\kappa^P}{\eta^S} Y\right) B^{*2}. \qquad (1.14)$$

For $T \geq T_D = 55$ K, Fitzgerald[4] showed that the efficiency parameters are close to their infinite-temperature limits, $\eta^S = 2686.8$ and $\eta^P = 8874.1$. For the same radial dependence of the antishielding used by Fitzgerald[4] ($\epsilon_0 = -11.8$), we find that the anisotropic efficiency has the high-temperature limit $\kappa^P = 6033.1$, so the relative rate $\mathcal{R}$ in Eq. (1.14) has the numerical value

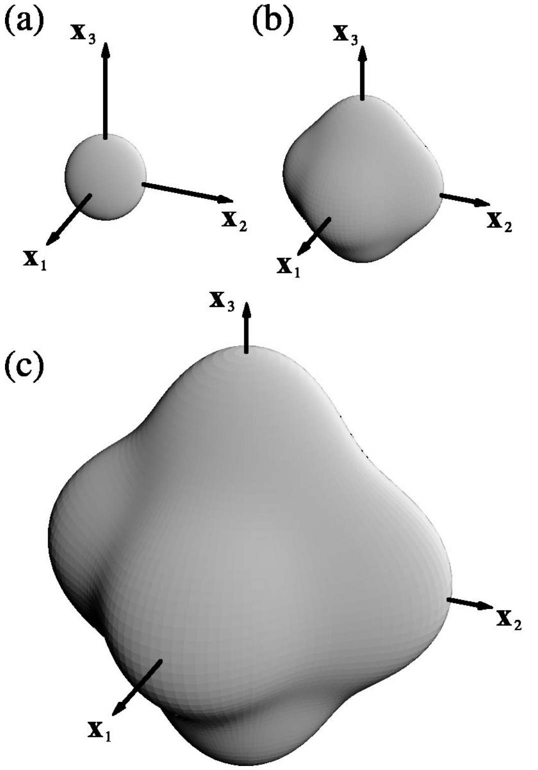

FIG. 3. The relative relaxation rate $\mathcal{R}$, given in Eq. (1.15), is plotted as a function of the direction of the applied magnetic field $\mathbf{B}_0$ with respect to the crystalline basis vectors $\mathbf{x}_1$, $\mathbf{x}_2$, and $\mathbf{x}_3$, for three different values of B_0: (a) $B_0 = 0$, (b) $B_0 = \frac{1}{2}B_D$, and (c) $B_0 = B_D$, where $B_D = k_B T_D/\mu_B = 82$ T for solid xenon.

$$\mathcal{R} = 1 + [3.303 + 2.245 Y(\theta, \phi)] B^{*2}. \qquad (1.15)$$

In Fig. 3 the magnitude of the relative relaxation rate $\mathcal{R}$ is plotted versus the applied field direction for several relative field values B^*. $Y(\theta, \phi)$ attains its maximum value $(\frac{2}{5})$ when $\mathbf{b}_3$ points toward one of the six faces of the cube of Fig. 1, and it attains its minimum value $(-\frac{4}{15})$ when $\mathbf{b}_3$ points toward one of the eight corners of the cube. The corresponding maximum and minimum values of $\mathcal{R}$ are $1 + 4.201 B^{*2}$ and $1 + 2.704 B^{*2}$. In the high-field limit, the maximum relaxation rate is a factor of 1.554 faster than the minimum relaxation rate.

Measuring the relaxation rate of ^{129}Xe spins in single crystals of xenon at fields of some tens of T would be the most direct test of the predictions of this paper. However, referees of this paper kindly pointed out that for polycrystalline samples with sufficiently large crystallites, the anisotropy effects should be observable as a nonexponential spin relaxation.[8,9] A similar dependence of the relaxation rate on the direction of the magnetic field should be observable in crystals containing the spin-1/2 isotope ^{207}Pb. These may be more convenient for experimental studies. The methods outlined below can be modified in a straightforward way to predict relaxation rates for other crystals with the same or different symmetry groups.

II. SINGLE-CRYSTAL SYMMETRY

As illustrated in Fig. 1(a), the 12 nearest-neighbor atoms of a ^{129}Xe atom can be located on the edges of a cube, with the ^{129}Xe atom (labeled α) in the center. A unit vector from the ^{129}Xe atom α to one of its nearest-neighbor atoms β is denoted by $\mathbf{n}_\beta$. From inspection, we find that the locations of the 12 nearest-neighbor atoms are transformed into each other, leaving the ^{129}Xe atom α fixed, by the operations of the symmetry group O_h of the cube.[11] The group O_h has $g=48$ elements and ten classes, and therefore $r=10$ irreducible representations $G_{ij}^{(\alpha)}$. The representations are labeled by the superscript (α). The representations of O_h are *gerade* and *ungerade* versions of the five irreducible representations of the octahedral group O. Following the convention of Landau and Lifshitz,[11] we will label the irreducible representations of O by the symbols $\alpha=A_1$, A_2, E, F_2, and F_1. The dimensions $f^{(\alpha)}$ of these representations are 1, 1, 2, 3, and 3, respectively.

Since the irreducible representations $G_{ij}^{(\alpha)}$ of O_h can be chosen to be real, we can write the fundamental orthogonality relation for irreducible representations α and β of the group O_h [see Eq. (94.8) in Landau and Lifshitz[11]] as

$$\frac{1}{g}\sum_G G_{ri}^{(\alpha)}G_{sj}^{(\beta)}=\frac{1}{f^{(\alpha)}}\delta_{\alpha\beta}\delta_{rs}\delta_{ij}. \tag{2.1}$$

The sum extends over all $g=48$ elements G of the group O_h.

As illustrated in Fig. 1(b), we let the externally applied magnetic field $\mathbf{B}_0$ define a set of orthonormal basis vectors $\mathbf{b}_i$, such that $\mathbf{b}_3=\mathbf{B}_0/B_0$, and $(\mathbf{b}_i\times\mathbf{b}_j)\cdot\mathbf{b}_k=\epsilon_{ijk}$ with ϵ_{ijk} being the antisymmetric unit tensor. The unit vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ can be any orthogonal pair that spans the plane perpendicular to $\mathbf{B}_0$. We can define the unnormalized circular basis vectors as

$$\mathbf{b}_\pm=\mathbf{b}_1\pm i\mathbf{b}_2. \tag{2.2}$$

According to Eq. (2.29) of Fitzgerald,[4] the fluctuation of the paramagnetic antishielding field is proportional to

$$\begin{aligned}\mathbf{w}'_\beta=\frac{1}{2\omega_D}\boldsymbol{\omega}_0\cdot\{&[\mathbf{b}_{j_e}\mathbf{b}_{j_a}+\mathbf{b}_{j_a}\mathbf{b}_{j_e}]+\epsilon_0[\mathbf{n}_\beta\cdot\mathbf{b}_{j_e}(\mathbf{n}_\beta\mathbf{b}_{j_a}+\mathbf{b}_{j_a}\mathbf{n}_\beta)\\&+\mathbf{n}_\beta\cdot\mathbf{b}_{j_a}(\mathbf{n}_\beta\mathbf{b}_{j_e}+\mathbf{b}_{j_e}\mathbf{n}_\beta)]+\epsilon_0[\mathbf{b}_{j_e}\cdot\mathbf{b}_{j_a}+(\epsilon_0-1)\\&\times(\mathbf{n}_\beta\cdot\mathbf{b}_{j_e})(\mathbf{n}_\beta\cdot\mathbf{b}_{j_a})]\mathbf{n}_\beta\mathbf{n}_\beta\}.\end{aligned} \tag{2.3}$$

The field results from the motion of atom β when a phonon of polarization $\mathbf{b}_{j_e}$ is emitted (with $j_e=1,2,3$) and a phonon of polarization $\mathbf{b}_{j_a}$ is absorbed.

Since the "field" [Eq. (2.3)] must be squared to calculate relaxation rates, the rates will be functions, which we denote by $f(\mathbf{n}_\beta,\mathbf{n}_\delta)$, of the unit vectors $\mathbf{n}_\beta$ and $\mathbf{n}_\delta$, pointing to two nearest-neighbor atoms β and δ. Since there are 12 nearest neighbors, the values of f will have to be summed for 144 nearest-neighbor pairs. To avoid summing such a large number of terms, we make use of the symmetry of the nearest neighbors under the group O_h to reduce each sum to five terms, one for each of the five sets Λ_m.

An element G of the group O_h will transform $\mathbf{n}_\beta$ into another unit vector $\mathbf{n}_{\beta'}=G\mathbf{n}_\beta$. Let the group transformations G rotate (or invert) the unit vectors $\mathbf{x}_i$, so that

$$G\mathbf{n}_\beta=\mathbf{n}_{\beta'}=G\sum_i n_{\beta i}\mathbf{x}_i=\sum_{ij} n_{\beta i}\mathbf{x}_j G_{ij}^{(F_1)}. \tag{2.4}$$

As implied in Eq. (2.4), $\mathbf{x}_i$ form a basis for the three dimensional irreducible representation F_1.

The transformation of a function $f=f(\mathbf{n}_\beta,\mathbf{n}_\delta)$ into a function $Gf=Gf(\mathbf{n}_\beta,\mathbf{n}_\delta)$, by an element G of the group, is defined by[11]

$$Gf(\mathbf{n}_\beta,\mathbf{n}_\delta)=f(G^{-1}\mathbf{n}_\beta,G^{-1}\mathbf{n}_\delta). \tag{2.5}$$

Here G^{-1} is the inverse group element to G. It is obvious that

$$\sum_{(\beta\delta)\in\Lambda_m} f(\mathbf{n}_\beta,\mathbf{n}_\delta)=g_m\langle f\rangle_m, \tag{2.6}$$

where g_m is the number of ordered pairs in Λ_m. The angular brackets indicate a group average

$$\langle f\rangle_m=\frac{1}{g}\sum_G Gf(\mathbf{n}_\beta,\mathbf{n}_\delta). \tag{2.7}$$

Applying each element G to $f(\mathbf{n}_\beta,\mathbf{n}_\delta)$ for *any* representative pair $(\beta\delta)\in\Lambda_m$, we will generate values of f for $g=48$ pairs, all members of the set Λ_m. Each pair will occur g/g_m times.

III. SPIN-ROTATION INTERACTION

As discussed in connection with Eq. (A1) of Fitzgerald,[4] to evaluate the relaxation due to Raman scattering of phonons through the spin-rotation interaction, we need to average values of a few simple dyads and tetrads. For a dyad of the form $\mathbf{n}_\beta\mathbf{n}_\delta$ we find

$$\begin{aligned}\langle\mathbf{n}_\beta\mathbf{n}_\delta\rangle_m&=\frac{1}{g}\sum_G G\mathbf{n}_\beta\mathbf{n}_\delta=\sum_{ijrs} n_{\beta i}n_{\delta j}\mathbf{x}_r\mathbf{x}_s\frac{1}{g}\sum_G G_{ri}^{(F_1)}G_{sj}^{(F_1)}\\&=\frac{1}{3}\mathbf{n}_\beta\cdot\mathbf{n}_\delta=\frac{1}{3}\cos\theta_m.\end{aligned} \tag{3.1}$$

We use the notation $n_{\beta i}=\mathbf{n}_\beta\cdot\mathbf{x}_i$. The average [Eq. (3.1)] over the group O_h is exactly the same as the average over the full rotation group given by Eq. (A7) of Fitzgerald. Similarly, we can write

$$\begin{aligned}&\langle(\mathbf{n}_\beta\times\mathbf{n}_\delta)(\mathbf{n}_\beta\times\mathbf{n}_\delta)\rangle_m\\&\quad=\sum_{abcd} n_{\beta a}n_{\delta b}n_{\beta c}n_{\delta d}\sum_{ijrs}\epsilon_{abi}\epsilon_{cdj}\mathbf{x}_r\mathbf{x}_s\frac{1}{g}\sum_G G_{ri}^{(F_1)}G_{sj}^{(F_1)}\\&\quad=\frac{1}{3}(\mathbf{n}_\beta\cdot\mathbf{n}_\beta\mathbf{n}_\delta\cdot\mathbf{n}_\delta-\mathbf{n}_\beta\cdot\mathbf{n}_\delta\mathbf{n}_\beta\cdot\mathbf{n}_\delta)=\frac{1}{3}\sin^2\theta_m.\end{aligned} \tag{3.2}$$

To simplify the evaluation of Eq. (3.2), we ignored the fact that cross products are pseudovectors, not true vectors. This makes no difference when an even number of vectors is involved, as in Eq. (3.2). The average [Eq. (3.2)] over the group O_h is exactly the same as the average over the full rotation group given by Eq. (A9) of Fitzerald.[4] Thus, expression (1.5) of Fitzgerald,[4] derived for a polycrystalline sample, remains valid for a single crystal. For Raman scattering of phonons by the spin-rotation interaction [Eq. (1.1)], there is no dependence of the rate on the direction of the externally applied magnetic field.

IV. PARAMAGNETIC ANTISHIELDING

Using Eq. (A12) of Fitzgerald,[4] we write

$$\mathbf{b}_+ \cdot \sum_{j_e j_a} \mathbf{w}'_\beta \mathbf{w}'_\delta \cdot \mathbf{b}_- = B^{*2} \sum_{i=1}^{6} X_i \,, \tag{4.1}$$

where

$$X_1 = \mathbf{b}_+ \cdot \frac{1}{2}(\mathbf{1} + \mathbf{b}_3\mathbf{b}_3) \cdot \mathbf{b}_- = 1, \tag{4.2}$$

$$X_2 = \frac{\epsilon_0}{2} \mathbf{b}_+ \cdot [(\mathbf{n}_\beta\mathbf{n}_\beta + \mathbf{n}_\delta\mathbf{n}_\delta) + \{\mathbf{b}_3 \cdot (\mathbf{n}_\beta\mathbf{n}_\beta + \mathbf{n}_\delta\mathbf{n}_\delta) \cdot \mathbf{b}_3\}\mathbf{1}] \cdot \mathbf{b}_- \,, \tag{4.3}$$

$$\begin{aligned} X_3 = \frac{\epsilon_0^2}{2} \mathbf{b}_+ \cdot [&(\mathbf{n}_\beta \cdot \mathbf{n}_\delta)(\{\mathbf{b}_3 \cdot \mathbf{n}_\beta\mathbf{n}_\delta \cdot \mathbf{b}_3\}\mathbf{1} + \mathbf{n}_\beta\mathbf{n}_\delta) \\ &+ \mathbf{b}_3 \cdot (\mathbf{n}_\beta\mathbf{n}_\beta\mathbf{n}_\delta\mathbf{n}_\delta + \mathbf{n}_\delta\mathbf{n}_\delta\mathbf{n}_\beta\mathbf{n}_\beta + \mathbf{n}_\beta\mathbf{n}_\delta\mathbf{n}_\delta\mathbf{n}_\beta \\ &+ \mathbf{n}_\delta\mathbf{n}_\beta\mathbf{n}_\beta\mathbf{n}_\delta) \cdot \mathbf{b}_3] \cdot \mathbf{b}_- \,, \end{aligned} \tag{4.4}$$

$$X_4 = \frac{\epsilon_0(\epsilon_0 - 1)}{2} \mathbf{b}_+ \cdot [\mathbf{b}_3 \cdot (\mathbf{n}_\beta\mathbf{n}_\beta\mathbf{n}_\beta\mathbf{n}_\beta + \mathbf{n}_\delta\mathbf{n}_\delta\mathbf{n}_\delta\mathbf{n}_\delta) \cdot \mathbf{b}_3] \cdot \mathbf{b}_- \,, \tag{4.5}$$

$$\begin{aligned} X_5 = \frac{\epsilon_0^2}{2} \mathbf{b}_+ \cdot [&(4\mathbf{b}_3 \cdot (\mathbf{n}_\beta\mathbf{n}_\beta\mathbf{n}_\delta\mathbf{n}_\delta) \cdot \mathbf{b}_3 \\ &+ (\epsilon_0 - 1)(\mathbf{n}_\beta \cdot \mathbf{n}_\delta)\mathbf{b}_3 \cdot (\mathbf{n}_\beta\mathbf{n}_\beta\mathbf{n}_\beta\mathbf{n}_\delta + \mathbf{n}_\beta\mathbf{n}_\beta\mathbf{n}_\delta\mathbf{n}_\beta \\ &+ \mathbf{n}_\delta\mathbf{n}_\beta\mathbf{n}_\delta\mathbf{n}_\delta + \mathbf{n}_\beta\mathbf{n}_\delta\mathbf{n}_\delta\mathbf{n}_\delta) \cdot \mathbf{b}_3] \cdot \mathbf{b}_- \,, \end{aligned} \tag{4.6}$$

$$\begin{aligned} X_6 = \frac{\epsilon_0^2}{4} \mathbf{b}_+ \cdot [&\mathbf{b}_3 \cdot (\mathbf{n}_\beta\mathbf{n}_\beta\mathbf{n}_\delta\mathbf{n}_\delta) \cdot \mathbf{b}_3\{3 + 2(\epsilon_0 - 1) \\ &+ (\epsilon_0 - 1)^2(\mathbf{n}_\beta \cdot \mathbf{n}_\delta)^2\}] \cdot \mathbf{b}_- \,. \end{aligned} \tag{4.7}$$

In Eqs. (4.2)–(4.7), the unit vectors $\mathbf{n}_\beta$ and $\mathbf{n}_\delta$ occur in the following combinations: (a) as scalar products like $\mathbf{n}_\beta \cdot \mathbf{n}_\delta$, which are invariant under group operations; (b) as dyadics like $\mathbf{n}_\beta\mathbf{n}_\delta$, which were averaged in the previous section; and (c) as tetrads of the form $\mathbf{n}_\kappa\mathbf{n}_\lambda\mathbf{n}_\rho\mathbf{n}_\sigma$. The indices $\kappa\lambda\rho\sigma$ are some combination of β and δ; for example we might have $\kappa\lambda\rho\sigma = \beta\beta\delta\delta$ or $\kappa\lambda\rho\sigma = \beta\beta\beta\delta$. The group average of a tetrad is

$$\begin{aligned} \langle \mathbf{n}_\kappa\mathbf{n}_\lambda\mathbf{n}_\rho\mathbf{n}_\sigma \rangle_m = &\sum_{ijkl} n_{\kappa i} n_{\lambda j} n_{\rho k} n_{\sigma l} \sum_{rstu} \mathbf{x}_r\mathbf{x}_s\mathbf{x}_t\mathbf{x}_u \\ &\times \frac{1}{g} \sum_G G_{ri}^{(F_1)} G_{sj}^{(F_1)} G_{tk}^{(F_1)} G_{ul}^{(F_1)} \,. \end{aligned} \tag{4.8}$$

There is no general way, analogous to Eq. (2.1), to evaluate the sum in Eq. (4.8). However it is not hard to solve the problem by coupling the unit vectors in pairs to form dyadic irreducible representations of O_h. The group average of the tetrads, products of the pairs, can then be evaluated with Eq. (2.1). This is similar to the pairwise coupling of unit vectors used in Appendix A of Fitzgerald[4] to evaluate the average of tetrads over the full rotation group.

Consider the reducible representation formed by the nine dyads $\mathbf{x}_i\mathbf{x}_j$. We denote linear combinations of the simple dyads $\mathbf{x}_i\mathbf{x}_j$ with the symbol $\mathcal{D}$ (for *dyadic*). We can choose nine orthonormal linear combinations of dyads $\mathbf{x}_i\mathbf{x}_j$ that span four irreducible subspaces, as follows.

A_1: This subspace generates the one-dimensional, identity representation A_1. It has the single basis dyadic

$$\mathcal{D}_1^{(A_1)} = \frac{\mathbf{1}}{\sqrt{3}}. \tag{4.9}$$

E: This subspace generates the two-dimensional representation E. The two basis dyadics can be chosen to be

$$\mathcal{D}_1^{(E)} = \frac{1}{\sqrt{6}}(3\mathbf{x}_3\mathbf{x}_3 - \mathbf{1}), \tag{4.10}$$

$$\mathcal{D}_2^{(E)} = \frac{1}{\sqrt{2}}(\mathbf{x}_1\mathbf{x}_1 - \mathbf{x}_2\mathbf{x}_2). \tag{4.11}$$

F_2: This subspace generates the three-dimensional, antisymmetric representation F_2. The three basis dyadics can be chosen to be

$$\mathcal{D}_1^{(F_2)} = \frac{1}{\sqrt{2}}(\mathbf{x}_2\mathbf{x}_3 - \mathbf{x}_3\mathbf{x}_2), \tag{4.12}$$

$$\mathcal{D}_2^{(F_2)} = \frac{1}{\sqrt{2}}(\mathbf{x}_3\mathbf{x}_1 - \mathbf{x}_1\mathbf{x}_3), \tag{4.13}$$

$$\mathcal{D}_3^{(F_2)} = \frac{1}{\sqrt{2}}(\mathbf{x}_1\mathbf{x}_2 - \mathbf{x}_2\mathbf{x}_1). \tag{4.14}$$

F_1: This subspace generates three-dimensional, symmetric representation F_1. The three basis dyadics can be chosen to be

$$\mathcal{D}_1^{(F_1)} = \frac{1}{\sqrt{2}}(\mathbf{x}_2\mathbf{x}_3 + \mathbf{x}_3\mathbf{x}_2), \tag{4.15}$$

TABLE I. Coupling coefficients $[n_\kappa n_\lambda]_\mu^{(\alpha)}$, defined in Eq. (4.19).

α	$\mu=1$	$\mu=2$	$\mu=3$
A_1	$\mathbf{n}_\beta\cdot\mathbf{n}_\delta/\sqrt{3}$		
E	$(3n_{\beta3}n_{\delta3}-\mathbf{n}_\beta\cdot\mathbf{n}_\delta)/\sqrt{6}$	$(n_{\beta1}n_{\delta1}-n_{\beta2}n_{\delta2})/\sqrt{2}$	
F_2	$(n_{\beta2}n_{\delta3}-n_{\beta3}n_{\delta2})/\sqrt{2}$	$(n_{\beta3}n_{\delta1}-n_{\beta1}n_{\delta3})/\sqrt{2}$	$(n_{\beta1}n_{\delta2}-n_{\beta2}n_{\delta1})/\sqrt{2}$
F_1	$(n_{\beta2}n_{\delta3}+n_{\beta3}n_{\delta2})/\sqrt{2}$	$(n_{\beta3}n_{\delta1}+n_{\beta1}n_{\delta3})/\sqrt{2}$	$(n_{\beta1}n_{\delta2}+n_{\beta2}n_{\delta1})/\sqrt{2}$

$$\mathcal{D}_2^{(F_1)}=\frac{1}{\sqrt{2}}(\mathbf{x}_3\mathbf{x}_1+\mathbf{x}_1\mathbf{x}_3), \tag{4.16}$$

$$\mathcal{D}_3^{(F_1)}=\frac{1}{\sqrt{2}}(\mathbf{x}_1\mathbf{x}_2+\mathbf{x}_2\mathbf{x}_1). \tag{4.17}$$

Writing the simple product dyads in terms of the irreducible dyads $\mathcal{D}_\mu^{(\alpha)}$ defined above, we find

$$\mathbf{n}_\kappa\mathbf{n}_\lambda=\sum_{\alpha\mu}[n_\kappa n_\lambda]_\mu^{(\alpha)}\mathcal{D}_\mu^{(\alpha)}, \tag{4.18}$$

where

$$[n_\kappa n_\lambda]_\mu^{(\alpha)}=\sum_{ij}n_{\kappa i}n_{\lambda j}C(\alpha\mu;F_1 i,F_1 j)=\mathbf{n}_\kappa\cdot\mathcal{D}_\mu^{(\alpha)}\cdot\mathbf{n}_\lambda. \tag{4.19}$$

The Clebsch-Gordan coefficients[12] $C(\alpha\mu;F_1 i,F_1 j)$ can be found from an inspection of Eqs. (4.9)–(4.17). For future reference, explicit expressions for the coefficients $[n_\kappa n_\lambda]_\mu^{(\alpha)}$ are summarized in Table I.

Using Eq. (4.18), we can write Eq. (4.8) as

$$\begin{aligned}\langle\mathbf{n}_\kappa\mathbf{n}_\lambda\mathbf{n}_\rho\mathbf{n}_\sigma\rangle_m&=\frac{1}{g}\sum_G G\sum_{\alpha\mu\beta\nu}[n_\kappa n_\lambda]_\mu^{(\alpha)}\mathcal{D}_\mu^{(\alpha)}[n_\rho n_\sigma]_\nu^{(\beta)}\mathcal{D}_\nu^{(\beta)}\\&=\sum_{\alpha\beta\mu\nu\mu'\nu'}[n_\kappa n_\lambda]_\mu^{(\alpha)}[n_\rho n_\sigma]_\nu^{(\beta)}\mathcal{D}_{\mu'}^{(\alpha)}\mathcal{D}_{\nu'}^{(\beta)}\\&\quad\times\frac{1}{g}\sum_G G_{\mu'\mu}^{(\alpha)}G_{\nu'\nu}^{(\beta)}\\&=\sum_\alpha\mathcal{T}^{(\alpha)}\sum_l N_l^{(\alpha)}(\kappa\lambda\rho\sigma)P_l.\end{aligned} \tag{4.20}$$

The sum on α extends over the irreducible representations A_1, E, F_2, and F_1. The representation A_2 does not occur. The tetradic is

$$\mathcal{T}^{(\alpha)}=\sum_\nu\mathcal{D}_\nu^{(\alpha)}\mathcal{D}_\nu^{(\alpha)}, \tag{4.21}$$

and the coefficient is

$$\sum_l N_l^{(\alpha)}(\kappa\lambda\rho\sigma)P_l=\frac{1}{f_\alpha}\sum_\mu[n_\kappa n_\lambda]_\mu^{(\alpha)}[n_\rho n_\sigma]_\mu^{(\alpha)}. \tag{4.22}$$

TABLE II. Coefficients $N_l^{(\alpha)}(\beta\beta\delta\delta)$, given in Eq. (4.22).

α	$l=0$	$l=2$	$l=4$
E	$-1/180$	$-4/63$	16/105
F_2	0	0	0
F_1	1/270	50/189	$-32/315$

To facilitate a comparison with the results of Fitzgerald,[4] where it was natural to describe the dependence of group averages on m by means of Legendre polynomials $P_l=P_l(\cos\theta_m)$, we use Legendre polynomial expansions in Eq. (4.22).

As we shall show below, there is no contribution to Eq. (4.1) from terms of Eq. (4.20) with $\alpha=A_1$, so we will ignore the coefficients $N_l^{(A_1)}(\kappa\lambda\rho\sigma)$. The values of $N_l^{(\alpha)}(\beta\delta\delta\delta)$, $N_l^{(\alpha)}(\delta\beta\delta\delta)$, $N_l^{(\alpha)}(\delta\delta\beta\delta)$, and $N_l^{(\alpha)}(\delta\delta\delta\beta)$ are all equal, and the nonzero values with $\alpha\neq A_1$ are

$$N_1^{(E)}(\beta\delta\delta\delta)=\frac{1}{12},\quad N_1^{(F_1)}(\beta\delta\delta\delta)=\frac{1}{6}. \tag{4.23}$$

The other coefficients $N_l^{(\alpha)}$ that we will need are summarized in Tables II and III.

V. GROUP AVERAGES $\langle X_i\rangle_m$

With the results of Sec. IV, we can now evaluate the group averages $\langle X_i\rangle_m$ of quantities (4.2)–(4.7). We will have to evaluate the quantities of the form

$$\begin{aligned}&\mathbf{b}_+\cdot\{\mathbf{b}_3\cdot\langle\mathbf{n}_\kappa\mathbf{n}_\lambda\mathbf{n}_\rho\mathbf{n}_\sigma\rangle_m\cdot\mathbf{b}_3\}\cdot\mathbf{b}_-\\&\quad=\sum_\alpha t^{(\alpha)}\sum_l N_l^{(\alpha)}(\kappa\lambda\rho\sigma)P_l,\end{aligned} \tag{5.1}$$

where we used Eq. (4.20) to define

$$t^{(\alpha)}=\mathbf{b}_+\cdot\{\mathbf{b}_3\cdot\mathcal{T}^{(\alpha)}\cdot\mathbf{b}_3\}\cdot\mathbf{b}_-. \tag{5.2}$$

We define matrix elements in the basis $\mathbf{b}_i$ by

TABLE III. Coefficients $N_l^{(\alpha)}(\beta\delta\delta\beta)$, given in Eq. (4.22).

α	$l=0$	$l=2$	$l=4$
E	19/180	$-11/63$	16/105
F_2	$-1/9$	1/9	0
F_1	31/270	29/189	$-32/315$

$$D^{(\alpha)}_{\nu;ij}=\mathbf{b}_i\cdot\mathcal{D}^{(\alpha)}_{\nu}\cdot\mathbf{b}_j . \tag{5.3}$$

From inspection of Eqs. (4.9)–(4.17), we see that

$$D^{(\alpha)}_{\nu;ij}=D^{(\alpha)}_{\nu;ji} \quad \text{if} \quad \alpha=A_1,E,F_1, \tag{5.4}$$

and

$$D^{(\alpha)}_{\nu;ij}=-D^{(\alpha)}_{\nu;ji} \quad \text{if} \quad \alpha=F_2 . \tag{5.5}$$

Using Eqs. (5.3)–(5.5), we can write Eq. (5.2) as

$$\begin{aligned}
t^{(\alpha)}=\mathbf{b}_+\cdot\{\mathbf{b}_3\cdot\mathcal{T}^{(\alpha)}\cdot\mathbf{b}_3\}\cdot\mathbf{b}_-&=\sum_{\nu}\ \mathbf{b}_3\cdot\mathcal{D}^{(\alpha)}_{\nu}\cdot\mathbf{b}_+\mathbf{b}_-\cdot\mathcal{D}^{(\alpha)}_{\nu}\cdot\mathbf{b}_3\\
&=\sum_{\nu}\ \{\mathcal{D}^{(\alpha)}_{\nu;31}+i\mathcal{D}^{(\alpha)}_{\nu;32}\}\{\mathcal{D}^{(\alpha)}_{\nu;13}-i\mathcal{D}^{(\alpha)}_{\nu;23}\}\\
&=\sum_{\nu}\ \{D^{(\alpha)}_{\nu;31}D^{(\alpha)}_{\nu;13}+D^{(\alpha)}_{\nu;32}D^{(\alpha)}_{\nu;23}\}\\
&\quad -i\sum_{\nu}\ \{D^{(\alpha)}_{\nu;31}D^{(\alpha)}_{\nu;23}-D^{(\alpha)}_{\nu;32}D^{(\alpha)}_{\nu;13}\}.
\end{aligned} \tag{5.6}$$

From Eqs. (5.4) and (5.5) we can see that the last term of Eq. (5.6) vanishes, so we have

$$\begin{aligned}
t^{(\alpha)}&=\sum_{\nu}\ \{D^{(\alpha)}_{\nu;31}D^{(\alpha)}_{\nu;13}+D^{(\alpha)}_{\nu;32}D^{(\alpha)}_{\nu;23}\\
&\quad +D^{(\alpha)}_{\nu;33}D^{(\alpha)}_{\nu;33}-D^{(\alpha)}_{\nu;33}D^{(\alpha)}_{\nu;33}\}\\
&=\mathbf{b}_3\cdot\left\{\sum_{\nu}\ \mathcal{D}^{(\alpha)}_{\nu}\mathcal{D}^{(\alpha)}_{\nu}\right\}\cdot\mathbf{b}_3-\sum_{\nu}\ \{D^{(\alpha)}_{\nu;33}\}^2.
\end{aligned} \tag{5.7}$$

One can readily verify from Eqs. (4.9)–(4.17) that

$$\sum_{\nu}\ \mathcal{D}^{(\alpha)}_{\nu}\mathcal{D}^{(\alpha)}_{\nu}=M^{(\alpha)}\mathbf{1}, \tag{5.8}$$

where

$$M^{(A_1)}=\frac{1}{3}, \quad M^{(E)}=\frac{2}{3}, \quad M^{(F_2)}=-1, \quad M^{(F_1)}=1. \tag{5.9}$$

Hence, Eq. (5.7) becomes

$$t^{(\alpha)}=M^{(\alpha)}-\sum_{\nu}\ \{\mathbf{b}_3\cdot D^{(\alpha)}_{\nu}\cdot\mathbf{b}_3\}^2. \tag{5.10}$$

Substituting values from Eqs. (5.9) and (4.9)–(4.17) into Eq. (5.10) and using $\mathbf{b}=\mathbf{b}_3$, we find

$$t^{(A_1)}=0, \tag{5.11}$$

$$\begin{aligned}
t^{(E)}&=2[(\mathbf{b}\cdot\mathbf{x}_2)^2(\mathbf{b}\cdot\mathbf{x}_3)^2+(\mathbf{b}\cdot\mathbf{x}_3)^2(\mathbf{b}\cdot\mathbf{x}_1)^2\\
&\quad +(\mathbf{b}\cdot\mathbf{x}_1)^2(\mathbf{b}\cdot\mathbf{x}_2)^2]\\
&=2(\sin^2\theta\cos^2\theta+\sin^4\theta\sin^2\phi\cos^2\phi),
\end{aligned} \tag{5.12}$$

$$t^{(F_2)}=-1, \tag{5.13}$$

$$\begin{aligned}
t^{(F_1)}&=(\mathbf{b}\cdot\mathbf{x}_1)^4+(\mathbf{b}\cdot\mathbf{x}_2)^4+(\mathbf{b}\cdot\mathbf{x}_3)^4\\
&=\sin^4\theta(\cos^4\phi+\sin^4\phi)+\cos^4\theta.
\end{aligned} \tag{5.14}$$

We note that

$$t^{(E)}+t^{(F_1)}=1. \tag{5.15}$$

Using Eqs. (5.11)–(5.15), we can rewrite Eq. (5.1) as

$$\begin{aligned}
&\mathbf{b}_+\cdot\{\mathbf{b}_3\cdot\langle\mathbf{n}_\kappa\mathbf{n}_\lambda\mathbf{n}_\rho\mathbf{n}_\sigma\rangle\cdot\mathbf{b}_3\}\cdot\mathbf{b}_-\\
&\quad=\sum_{l}\ [a_l(\kappa\lambda\rho\sigma)+t^{(E)}b_l(\kappa\lambda\rho\sigma)]P_l ,
\end{aligned} \tag{5.16}$$

with

$$a_l(\kappa\lambda\rho\sigma)=N^{(F_1)}_l(\kappa\lambda\rho\sigma)-N^{(F_2)}_l(\kappa\lambda\rho\sigma), \tag{5.17}$$

$$b_l(\kappa\lambda\rho\sigma)=N^{(E)}_l(\kappa\lambda\rho\sigma)-N^{(F_1)}_l(\kappa\lambda\rho\sigma). \tag{5.18}$$

Explicit values of the coefficients a_l and b_l follow from Tables II and III; the nonzero values are

$$\begin{bmatrix} a_0(\beta\beta\delta\delta)\\ a_2(\beta\beta\delta\delta)\\ a_4(\beta\beta\delta\delta)\end{bmatrix}=\begin{bmatrix}1/270\\ 50/189\\ -32/315\end{bmatrix},$$

$$\begin{bmatrix} b_0(\beta\beta\delta\delta)\\ b_2(\beta\beta\delta\delta)\\ b_4(\beta\beta\delta\delta)\end{bmatrix}=\begin{bmatrix}-1/108\\ -62/189\\ 16/63\end{bmatrix}. \tag{5.19}$$

We find that $b_l(\beta\delta\delta\beta)=b_l(\beta\beta\delta\delta)$, and

$$\begin{bmatrix} a_0(\beta\delta\delta\beta)\\ a_2(\beta\delta\delta\beta)\\ a_4(\beta\delta\delta\beta)\end{bmatrix}=\begin{bmatrix}61/270\\ 8/189\\ -32/315\end{bmatrix}. \tag{5.20}$$

Values of a_l for $\kappa\lambda\mu\nu=\beta\beta\beta\delta$, $\beta\beta\delta\beta$, $\beta\delta\beta\beta$, or $\delta\beta\beta\beta$ are identical, and the same is true for b_l. The nonzero values are

$$a_1(\beta\beta\beta\delta)=1/6 \quad \text{and} \quad b_1(\beta\beta\beta\delta)=-1/12. \tag{5.21}$$

We are now in a position to evaluate the quantities $\langle X_i\rangle_m$ from Eqs. (4.2)–(4.7). For convenience in comparing with the work of Fitzgerald,[4] we will write

$$\langle X_i\rangle_m=\sum_{l}\ (p_{il}+t^{(E)}q_{il})P_l . \tag{5.22}$$

Using Eqs. (3.1), (4.2), and (4.3), we find

$$\langle X_1\rangle_m=p_{10}=1, \tag{5.23}$$

$$\langle X_2\rangle_m=p_{20}=\frac{4\epsilon_0}{3}. \tag{5.24}$$

As an example of how to average quantities containing factors (5.1), we sketch the evaluation of $\langle X_3\rangle_m$. From Eqs. (3.1), (4.4), and (5.16) we find

$$\langle X_3\rangle_m=\frac{\epsilon_0^2}{2}\left[\frac{4}{3}\cos^2\theta_m+\sum_l \{2a_l(\beta\beta\delta\delta)+2a_l(\beta\delta\delta\beta) + 4t^{(E)}b_l(\beta\beta\delta\delta)\}P_l(\cos\theta_m)\right]. \tag{5.25}$$

Noting the simple Legendre identity $x^2=(2/3)P_2(x)+(1/3)$, and using coefficients (5.19) and (5.20) in Eq. (5.25), we find the nonzero coefficients of Eq. (5.22) for $i=3$,

$$\begin{bmatrix} p_{30}\\ p_{32}\\ p_{34}\end{bmatrix}=\epsilon_0^2\begin{bmatrix} 61/135\\ 142/189\\ -64/315\end{bmatrix},\quad \begin{bmatrix} q_{30}\\ q_{32}\\ q_{34}\end{bmatrix}=\epsilon_0^2\begin{bmatrix} -1/54\\ -124/189\\ 32/63\end{bmatrix}. \tag{5.26}$$

The remaining nonzero coefficients for $i=4$, 5, and 6 can be calculated in a similar way, and they are

$$p_{40}=\frac{\epsilon_0(\epsilon_0-1)}{6} \quad \text{and} \quad q_{40}=-\frac{\epsilon_0(\epsilon_0-1)}{12}; \tag{5.27}$$

$$\begin{bmatrix} p_{50}\\ p_{52}\\ p_{54}\end{bmatrix}=\epsilon_0^2\begin{bmatrix} (15\epsilon_0-14)/135\\ (42\epsilon_0+58)/189\\ -64/315\end{bmatrix}, \tag{5.28}$$

$$\begin{bmatrix} q_{50}\\ q_{52}\\ q_{54}\end{bmatrix}=\epsilon_0^2\begin{bmatrix} (-3\epsilon_0+2)/54\\ (-21\epsilon_0-103)/189\\ 32/63\end{bmatrix}, \tag{5.29}$$

$$\begin{bmatrix} p_{60}\\ p_{62}\\ p_{64}\\ p_{66}\end{bmatrix}=\frac{\epsilon_0^2}{4}\begin{bmatrix} (138\epsilon_0^2-248\epsilon_0+152)/3780\\ (46\epsilon_0^2+108\epsilon_0+146)/378\\ (136\epsilon_0^2-976\epsilon_0-216)/3465\\ (-64\epsilon_0^2+128\epsilon_0-64)/2079\end{bmatrix}, \tag{5.30}$$

$$\begin{bmatrix} q_{60}\\ q_{62}\\ q_{64}\\ q_{66}\end{bmatrix}=\frac{\epsilon_0^2}{4}\begin{bmatrix} (-177\epsilon_0^2+284\epsilon_0-212)/3780\\ (-49\epsilon_0^2-150\epsilon_0-173)/378\\ (56\epsilon_0^2+1648\epsilon_0+936)/3465\\ (160\epsilon_0^2-320\epsilon_0+160)/2079\end{bmatrix}. \tag{5.31}$$

Using Eqs. (5.22), (4.1), and (2.6), and omitting constant factors, we can write Eq. (2.44) of Fitzgerald[4] as

$$\sum_m D'_m \sum_{(\beta\delta)\in\Lambda_m} \mathbf{b}_+\cdot\sum_{j_e j_a}\langle \mathbf{w}'_\beta\mathbf{w}'_\delta\rangle\cdot\mathbf{b}_-=B^{*2}(\eta^P+\kappa^P Y), \tag{5.32}$$

where, in agreement with Eq. (2.47) of Fitzgerald,[4] the isotropic efficiency coefficient is

$$\eta^P=\eta^P(\epsilon_0,T^*)=\sum_{ml} g_m c'_l P_l D'_m. \tag{5.33}$$

The sum extends over the set indices $m=0$, 1, 2, 3, and 4 with $g_m=12$, 48, 24, 48, and 12, respectively, in accordance with Table I of Fitzgerald.[4] The sum on Legendre polynomials includes the indices $l=0$, 2, and 4. The Legendre polynomials $P_l=P_l(\cos\theta_m)$ are implicit functions of m. The coefficients $c'_l=\Sigma_i(p_{il}+\frac{2}{5}q_{il})$ are identical to those of Eq. (5.34) of Fitzgerald.[4]

The anisotropic efficiency of Eq. (5.32) is

$$\kappa^P=\kappa^P(\epsilon_0,T^*)=\sum_{lm} g_m d'_l P_l D'_m. \tag{5.34}$$

The sum on Legendre polynomials now includes the indices $l=0$, 2, 4, and 6. The nonzero coefficients $d'_l=-\Sigma_i q_{il}$ are

$$\begin{bmatrix} d'_0\\ d'_2\\ d'_4\\ d'_6\end{bmatrix}=\begin{bmatrix} (177\epsilon_0^4+556\epsilon_0^3+1192\epsilon_0^2-1260\epsilon_0)/15120\\ (49\epsilon_0^4+318\epsilon_0^3+1989\epsilon_0^2)/1512\\ (-14\epsilon_0^4-412\epsilon_0^3-3754\epsilon_0^2)/3465\\ -40\epsilon_0^2(\epsilon_0-1)^2/2079\end{bmatrix}. \tag{5.35}$$

The function that describes how the relaxation rate depends on the direction **b** of the applied field relative to the crystal axes is

$$Y=Y(\mathbf{b})=\frac{2}{5}-t^{(E)}, \tag{5.36}$$

which together with Eqs. (5.14) and (5.15), gives Eq. (1.5). Summing Eqs. (5.33) and (5.34) over l gives expressions (1.8) and (1.12).

VI. DIRECT SUMMATION WITHOUT USING GROUP AVERAGES

To check the results of calculations presented in Secs. I and V, term-by-term evaluations of the sums needed to obtain the relaxation rates were carried out using the symbolic calculation package MATHEMATICA, version 3.0. The coefficients presented in Eqs. (1.9) and (1.13) were thus independently verified without resorting to group theory.

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