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Spin-Lattice Relaxation in Ruby*

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Spin-lattice relaxation times for ruby of very low Cr concentration at low temperature are computed for the one-phonon Kronig–Van Vleck process, using the spin-lattice Hamiltonian derived by Van Vleck and taking the vibrational anisotropy of the crystal into account. The relaxation times are computed as functions of the angle between the applied magnetic field and the *c* axis, temperature, and frequency. Reasonably good agreement with experimentally determined relaxation times is obtained.

I. INTRODUCTION

IN electron spin-lattice relaxation at low temperature, the dominant process should be the one-phonon process proposed by Kronig[1] and by Van Vleck,[2] which takes place through the combined effects of orbit-lattice coupling and spin-orbit coupling. In order to calculate the relaxation rate due to such a process, Van Vleck[2] employed an effective spin-lattice coupling Hamiltonian which is quadratic in spin and linear in lattice strain. Although Van Vleck's calculations pertained only to titanium and chromium, it was shown later by Mattuck and Strandberg[3] that such a spin-lattice Hamiltonian should be applicable to most iron-group ions. Estimates of spin-lattice relaxation times due to this interaction made originally by Van Vleck,[2] and later by Mattuck and Strandberg[3] and by Orbach[4] indicated that the proposed interaction does account for the observed spin-lattice relaxation times. This paper is concerned with a more accurate computation of spin-lattice relaxation times based on recent experimental work in which the spin-lattice interaction Hamiltonian has been measured, both by microwave ultrasonic techniques[5–7] and by observing the effects of uniaxial stress on electron spin resonance spectra.[8,9]

As a result of such measurements, the phonon-induced spin-transition probabilities for the one-phonon process can be computed and used to compute the spin-lattice relaxation times due to this process. This paper presents such a computation for the case of ruby (Al_2O_3:Cr^{3+}), assuming such a small Cr concentration that interactions between neighboring Cr ions may be neglected. Ruby was chosen for this computation because of its many important applications and also because the results are more interesting for this four-level system with zero-field splitting than for, say, the case of a simple Kramers doublet. Relaxation in such a system is, in general, characterized by three relaxation times, and, because of the zero-field splitting, these relaxation times depend strongly upon the angle between the applied magnetic field and the trigonal axis of the ruby.

Spin-lattice relaxation times in ruby have been extensively investigated, but most measurements have been carried out with samples of such high chromium concentration that exchange interactions and cross relaxation are important, resulting in strongly concentration-dependent relaxation times much shorter than those computed here. Measurements on samples of very low chromium concentration ($\leq 0.01\%$) are, however, in fair agreement with the results presented here, indicating that for such samples the Kronig–Van Vleck one-phonon process is dominant.

II. SPIN-LATTICE HAMILTONIAN

Van Vleck[2] originally derived the spin-lattice interaction Hamiltonian as a spin operator quadratic in spin and linear in strain. The most general expression for such an operator was first presented by Watkins and Feher[8] in the following form:

$$H_{\mathrm{SL}} = \sum_{i,j} D_{ij} S_i S_j . \tag{1}$$

The tensor D is related to strain linearly as follows:

$$D_{ij} = \sum_{i,j,k,l} G_{ijkl} e_{kl} . \tag{2}$$

The tensor G has many of the symmetry properties of

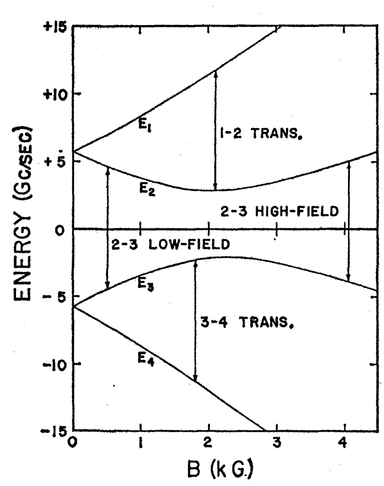

FIG. 1. Energy levels in ruby; $\theta = 50°$.

* Supported in part by NASA Grant Ns-G6-59.
[1] R. Kronig, Physica 6, 33 (1939).
[2] J. H. Van Vleck, Phys. Rev. 57, 426 (1940).
[3] R. D. Mattuck and M. W. P. Strandberg, Phys. Rev. 119, 1204 (1960).
[4] R. Orbach, thesis, University of California, 1960 (unpublished).
[5] E. B. Tucker, Phys. Rev. Letters 6, 183 (1961).
[6] N. S. Shiren, Bull. Am. Phys. Soc. 7, 29 (1962).
[7] R. N. Claytor, P. L. Donoho, and B. Josephson, Jr., Bull. Am. Phys. Soc. 7, 15 (1962).
[8] G. D. Watkins and E. Feher, Bull. Am. Phys. Soc. 7, 29 (1962).
[9] P. L. Donoho and R. B. Hemphill, Bull. Am. Phys. Soc. 7, 306 (1962).

the elastic stiffness tensor, limiting therefore the number of independent components. Furthermore, since D can be chosen to be traceless an added limitation is placed upon the number of independent components of G.

Although the maximum point-group symmetry of the Al_2O_3 lattice is D_{3d}, that at each chromium site is only C_3. Thus, there are two nonequivalent sets of chromium sites, each of which can be transformed into the other by means of a twofold rotation of the group D_{3d}. As a result, there are two different G tensors each of the form (in Voigt notation):

$$G=\begin{bmatrix} G_{11} & G_{12} & -G_{33}/2 & G_{14} & -G_{25} & G_{16} \\ G_{12} & G_{11} & -G_{33}/2 & -G_{14} & G_{25} & -G_{16} \\ -(G_{11}+G_{12}) & -(G_{11}+G_{12}) & G_{33} & 0 & 0 & 0 \\ G_{41} & -G_{41} & 0 & G_{44} & G_{45} & G_{52} \\ -G_{52} & G_{52} & 0 & -G_{45} & G_{44} & G_{41} \\ -G_{16} & G_{16} & 0 & G_{25} & G_{14} & \frac{1}{2}(G_{11}-G_{12}) \end{bmatrix}. \tag{3}$$

For the two different sites the components G_{11}, G_{12}, G_{33}, G_{44}, G_{14}, and G_{41} are respectively equal, whereas the components G_{25}, G_{52}, G_{16}, and G_{45} are equal, respectively, in magnitude but of opposite sign. The values obtained by Hemphill and Donoho[10] are given below:

$G_{11}=124.6$ Gc/sec	$G_{41}=-15.0$ Gc/sec
$G_{12}=-35.8$ Gc/sec	$G_{25}=45.0$ Gc/sec
$G_{33}=181.2$ Gc/sec	$G_{52}=45.0$ Gc/sec
$G_{44}=54.0$ Gc/sec	$G_{16}=0$
$G_{14}=-15.0$ Gc/sec	$G_{45}=0.$

In the following computation it is assumed that both sites are equally populated.

III. PHONON-INDUCED STRAIN

In order to obtain a reasonably accurate approximation to the phonon-induced lattice strain only frequencies for which the phonon wavelength is long compared to interatomic spacing will be considered. Thus it may be assumed that all atoms in a unit cell undergo displacements of equal amplitude. The displacement for phonons of wave vector $\mathbf{k}$ and polarization vector $\boldsymbol{\varepsilon}_p$ can therefore be written[11]

$$\mathbf{u}(\mathbf{r})=(\hbar/2M\omega)^{1/2}(a^{\dagger}_{k,p}-a_{-k,p})\boldsymbol{\varepsilon}_p e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{4}$$

where M is the crystal mass, ω is the phonon angular frequency, and the phonon operators a and $a^{\dagger}$ have the following properties:

$$a_{k,p}{}^{\dagger}|n_{k,p}\rangle=[(n_{k,p}+1)\hbar\omega]^{1/2}|n_{k,p}+1\rangle, \tag{5}$$

$$a_{k,p}|n_{k,p}\rangle=(n_{k,p}\hbar\omega)^{1/2}|n_{k,p}-1\rangle. \tag{6}$$

The strain due to this displacement is then obtained from the usual classical definition

$$e_{ij}=\frac{1}{2}\left(\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right). \tag{7}$$

Thus, the phonon strain can be written:

$$e_{ij}=(\hbar/8M\omega)^{1/2}(a_{k,p}{}^{\dagger}-a_{-k,p}), \times(\epsilon_{p,i}k_j+\epsilon_{p,j}k_i)e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{8}$$

In the calculation of spin-lattice transition probabilities the density of phonon states is required. For phonons with wave vector within solid angle $d\Omega$, this density is given by the following expression:

$$\rho(E)=V\omega^2 d\Omega/8\pi^3\hbar v_{k,p}, \tag{9}$$

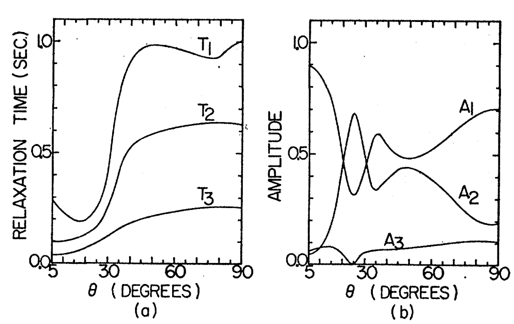

FIG. 2. Relaxation times and amplitudes for 1–2 trans.; $f=9.3$ Gc/sec, $T=4.2$°K.

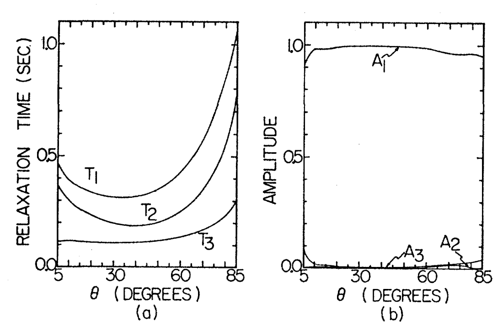

FIG. 3. Relaxation times and amplitudes for 2–3 (high-field) transition; $f=9.3$ Gc/sec, $T=4.2$°K.

[10] R. B. Hemphill and P. L. Donoho (to be published).

[11] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, 1959), Chap. 3.

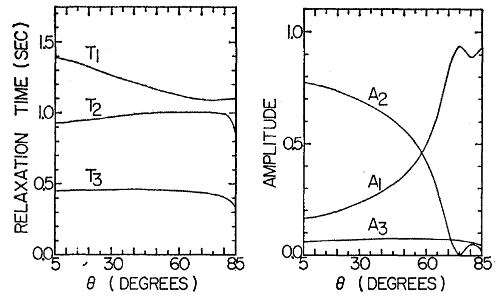

FIG. 4. Relaxation times and amplitudes for 2–3 (low-field) transition; $f=9.3$ Gc/sec, $T=4.2$°K.

where V is the crystal volume and $v_{k,p}$ is the phonon phase velocity, which depends upon both the direction of $\mathbf{k}$ and $\boldsymbol{\varepsilon}_p$.

Finally, it is assumed that the average phonon occupation number is given by the Bose-Einstein formula:

$$\bar{n}_{k,p}=(e^{\hbar\omega/kT}-1)^{-1}. \tag{10}$$

IV. SPIN-LATTICE TRANSITION PROBABILITY

The transition probability per unit time for a transition in which the ion goes from state i to state j and a phonon mode of frequency $\omega=(E_i-E_j)/\hbar$ goes from occupation number n to $n+1$ is obtained in the usual way from time-dependent perturbation theory. Because of the vibrational anisotropy of the crystal, the transition probability must be computed as a sum over all phonon polarizations and an integral over all directions of the phonon wave vector:

$$W_{ij}=\frac{\omega e^{\hbar\omega/kT}}{32\pi^2\rho\hbar(e^{\hbar\omega/kT}-1)}\int\sum_{p=1}^{3}\left|\sum_{m,n,s,t}G_{mnst}\langle i|s_ms_n|j\rangle\right.$$
$$\left.\times(\epsilon_{p,s}k_t+\epsilon_{p,t}k_s)\right|^2\frac{d\Omega}{v_{k,p}^{\;3}}. \tag{11}$$

This expression must be computed numerically using a high speed computer. For each direction of $\mathbf{k}$ the Christoffel equations must be solved for the phonon velocities and polarizations. In this computation the elastic constants obtained by Wachtman *et al.*[12] were used.

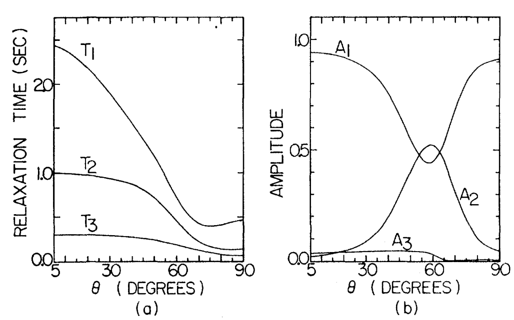

FIG. 5. Relaxation times and amplitudes for 3–4 transition; $f=9.3$ Gc/sec, $T=4.2$°K.

For each direction of the applied magnetic field with respect to the trigonal axis the matrix elements of the quadratic spin operators must also be computed. A simplified spin Hamiltonian of the form

$$H_S=g\beta\mathbf{H}\cdot\mathbf{S}+D(S_z^2-5/4) \tag{12}$$

was employed with isotropic $g=1.980$ and $D=-5.733$ Gc/sec. It is known from ultrasonic spin-resonance absorption measurements[6,7] that the computed matrix elements of quadratic spin operators between eigenstates of (12) are substantially correct.

Transition probabilities have been computed for all six transitions for many different values of frequency and for different angles between the applied field and the trigonal axis, but they are not presented here. Rather they are used to calculate relaxation times, which are more accessible to measurement, and therefore, more interesting. The transition probabilities themselves could be employed to predict such things as population inversion in maser applications, although they are only useful for crystals of very low chromium concentration.

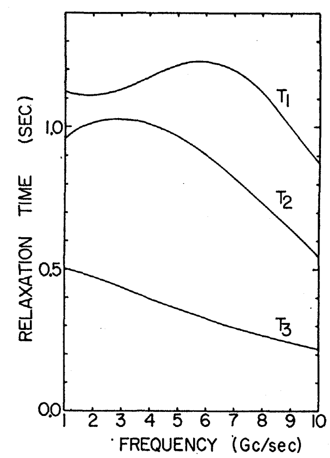

FIG. 6. Frequency dependence of relaxation times for 1–2 transition; $\theta=60°$, $T=4.2$°K.

V. SPIN-LATTICE RELAXATION TIMES

The transition probabilities for the six pairs of levels in the four-level Cr^{3+} ion are used to solve the rate equations which govern the dynamical behavior of the spin system. If the population of level j is denoted by n_j, these equations take the form

$$\dot{n}_i=\sum_{j=1}^{4}(W_{ji}n_j-W_{ij}n_i)\,,\quad i=1,2,3,4. \tag{13}$$

Such a set of equations will, in general, yield three in-

[12] J. B. Wachtman, Jr., W. E. Tefft, D. G. Lam, Jr., and R. P. Stinchfield, J. Res. Natl. Bur. Std. **64A**, 213 (1960).

dependent relaxation times, and the approach of the system to equilibrium after, say, saturation of a pair of levels will generally depend upon all three relaxation times.

For the results presented here it is assumed that a pair of levels is initially saturated and that the recovery of these levels to equilibrium is observed after removal of the saturating signal. Thus, the normalized population difference will have the form:

$$S=(n_i-n_j)/(n_{i0}-n_{j0})=1+A_1e^{-t/T_1}+A_2e^{-t/T_2}+A_3e^{-t/T_3}, \quad (14)$$

where n_i and n_j are the instantaneous populations of levels i and j, respectively, and n_{i0} and n_{j0} are their respective equilibrium values. The quantity S is then proportional to the signal observed in a typical recovery-after-saturation measurement. Of course, the levels involved in the recovery-after-saturation observation may be different from the saturated levels, but for simplicity the results presented here concern saturation and recovery of the same pair of levels.

Since the energy eigenvalues of the spin Hamiltonian (12) and its eigenfunctions depend strongly upon the angle θ between the trigonal axis and the applied magnetic field the quadratic spin matrix elements depend strongly upon this angle, with a resultant angular dependence of the relaxation times. For reference, Fig. 1 shows the energy levels of ruby and the nomenclature used here for referring to the levels.

The relaxation times T_1, T_2, and T_3 and the amplitudes A_1, A_2, and A_3 of Eq. (14) are illustrated in Figs. 2 through 5 for the 1–2, 2–3, and 3–4 transitions at a frequency of 9.3 Gc/sec as functions of θ.

It is seen that in most cases one relaxation time, usually the longest, dominates the behavior; when two relaxation times are important they are usually nearly equal. As a result it may be difficult experimentally to observe the mixture of different relaxation times in the recovery of a signal after saturation. If a transition of higher frequency, however, is saturated, say the 1–3 transition, and the recovery of a transition of lower frequency is observed, say the 2–3 transition, the shorter relaxation times become more important in general.

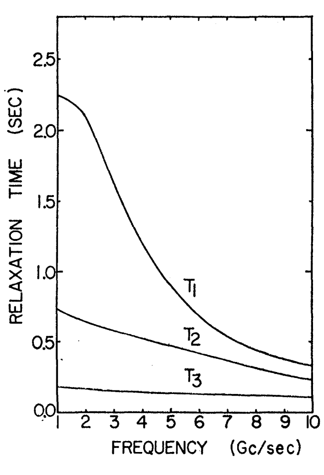

FIG. 7. Frequency dependence of relaxation times for 2–3 (high-field) transition; $\theta=20°$, $T=4.2°$K.

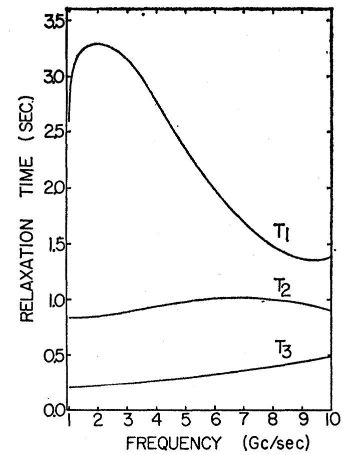

FIG. 8. Frequency dependence of relaxation times for 2–3 (low-field) transition; $\theta=20°$, $T=4.2°$K.

It is easy to explain the strong angular dependence of the relaxation times of, say, the 1–2 transition, illustrated in Fig. 2. At angles near zero the magnetic field is large (~7.5 kG); state 1 is largely $m_s=\frac{3}{2}$, and state 2 is largely $m_s=\frac{1}{2}$. The matrix elements of quadratic spin operators are large between these states, resulting in a large transition probability. At angles near 90°, however, the field is small (~1.5 kG); state 1 is largely $m_s=\frac{1}{2}$ and state 2 is largely $m_s=-\frac{1}{2}$, yielding very small matrix elements and, hence, small transition probability.

The frequency dependence of the relaxation times is interesting largely because it exhibits no definite behavior. Figures 6 through 9 illustrate the frequency dependence over the range 1–10 Gc/sec for 1–2, 2–3, and 3–4 transitions. These results are in agreement with those of several authors obtained over a frequency range[13–17] 3 Gc/sec–34 Gc/sec in which no strong frequency dependence is observed. It should be noted, however, that for a four-level Kramers system with no zero-field splitting the frequency dependence should be $(\omega)^{-2}$, whereas an isolated Kramers doublet would exhibit a dependence $(\omega)^{-4}$. The frequency dependence is therefore small mainly because of the zero-field splitting. Even though each transition probability is proportional to ω^2, the zero-field splitting provides, at least for small fields, the major contribution to the energy difference between levels such as 2 and 3 or 1 and 3 so that the corresponding transition probability will not depend greatly on the field and, hence, on frequency.

The temperature dependence of the relaxation times is not very interesting, being governed almost entirely

[13] W. B. Mims and J. D. McGee, Phys. Rev. **119**, 1233 (1960).
[14] R. A. Armstrong and A. Szabo, Can. J. Phys. **38**, 1304 (1960).
[15] Y. Nisida, J. Phys. Soc. Japan **17**, 1519 (1962).
[16] J. H. Pace, D. F. Sampson, and J. S. Thorp, Proc. Phys. Soc. (London) **76**, 697 (1960).
[17] S. Feng and N. Bloembergen, Phys. Rev. **130**, 531 (1963).

by the Bose-Einstein factor in the transition probability. Thus, since no allowance has been made in the computation for such effects as a phonon bottleneck the relaxation times almost always approach a constant value as temperature approaches zero. The case of the 3–4 transition is, however, different since it resembles the situation envisioned for rare-earth ions by Orbach[18] in which a ground-state doublet is separated from an excited state by an energy less than kT. In this case the direct transition probability W_{34} for small magnetic fields is very small compared to W_{14}, W_{24}, W_{13}, and W_{23} so that the relaxation rate for levels 3 and 4 is governed almost entirely by the populations of levels 1 and 2, which decrease exponentially with temperature. This situation is illustrated in Fig. 10, in which one relaxation time, that dominating the behavior of the 3–4 transition, increases almost exponentially with decreasing temperature while the others are constant.

The quantitative agreement between the computed relaxation times and experimentally measured values[13–17] is quite good, but only if measurements on samples containing much above 0.01% Cr are excluded. A comparison is presented between experimental results for such samples and computed values in Table I. Detailed measurements on ruby containing 0.005% Cr are in progress in this laboratory, but have not yielded usable results as yet.

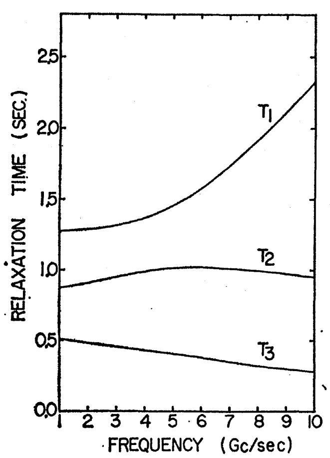

Fig. 9. Frequency dependence of relaxation times for 3–4 transition; $\theta=20°$, $T=4.2°$K.

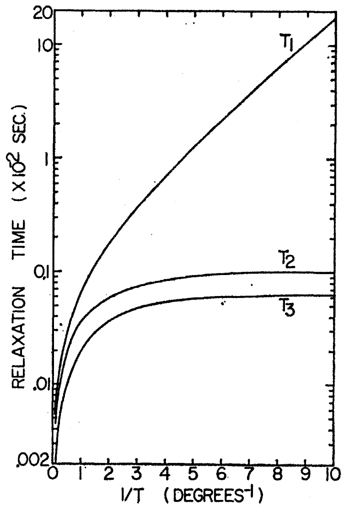

Fig. 10. Temperature dependence of relaxation times; $\theta=35°$, $B=0.415$ kG.

In conclusion it appears that the Kronig–Van Vleck mechanism adequately explains spin-lattice relaxation in ruby of sufficiently low Cr concentration. The results obtained here exhibit interesting features which are in reasonable agreement with experimental results, but which have not yet been verified in detail.

Table I. Comparison of calculated and experimental relaxation times in ruby.

Transition	θ deg	Freq. Gc/sec	T_R(calc) sec	T_R(exptl) sec
23	54	9.3	0.226	0.200[15]
23	80	7.2	0.539	0.500[13]
12	60	2.9	0.750	0.500[14]
13	90	34.6	0.080	0.054[16]

ACKNOWLEDGMENT

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[18] R. Orbach, Proc. Phys. Soc. (London) 77, 821 (1961).