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Direct One-Phonon Spin-Lattice Relaxation Times
for Nd^{3+} and U^{3+} Ions in CaF_2 in Sites
of Tetragonal Symmetry[†]

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Abstract

By utilizing the spin-lattice Hamiltonian measured by Black and Donoho for U^{3+} and Nd^{3+} ions in sites of tetragonal symmetry in CaF_2 , we have calculated the direct one-phonon spin-lattice relaxation times for these ions at low temperatures and microwave frequencies. Although fair agreement with experimental values is obtained for U^{3+} ions, the calculations yield values as much as a factor of 10^5 larger than the experimental values for Nd^{3+} ions. This disagreement is surprising in view of the fact that the same method of computation leads to very good agreement with experiment in the case of the iron-group ions. The possibility of other mechanisms of relaxation than the Van Vleck direct mechanism is considered in this paper.

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Spin-lattice relaxation of lanthanide- and actinide-group ions has been extensively studied both theoretically and experimentally in various materials. Perhaps the most striking feature of the spin-lattice relaxation process for these ions is the relaxation mechanism first proposed by Orbach (1961), which is a two-phonon process involving excited states of the relaxation ion. This Orbach process leads to an exponential temperature dependence of the relaxation time, and has led to considerable useful information concerning the excited states of rare-earth ions in various environments. The direct one-phonon relaxation mechanism, which should be dominant at very low temperature, is, however, also of interest, since for many ions the relaxation levels form a Kramers doublet. The spin-lattice interaction Hamiltonian for a Kramers doublet has been shown by Black and Donoho (1966) to be linear in the effective spin for certain ions, in contrast to the quadratic spin-lattice Hamiltonian which has been extensively employed to explain one-phonon spin-lattice relaxation for the iron-group ions. It is the purpose of this paper to use the spin-lattice



Hamiltonian formulation to compute the relaxation time for U^{3+} and Nd^{3+} ions in CaF_2 , and to compare the computed values with experimentally determined values.

The method of computation used here for the ions under consideration was first employed by Donoho (1964) for the case of Cr^{3+} ions in Al_2O_3 . The computed relaxation times for that case agree quite well with those measured by Standley and Vaughn (1965). For the present case, namely relaxation involving a Kramers doublet, the problem is somewhat simpler, and the method of computation is outlined briefly here.

The relaxation time, T_1 , is simply related to the phonon-induced transition probability between the two levels, W_{ij} , in the following well known manner:

$$1/T_1 = W_{12} + W_{21}$$

The transition probability is regarded as due to a perturbation Hamiltonian of the form introduced by Black and Donoho (1966). If the usual time-dependent perturbation theory is used, the expression for the transition probability takes the following form:

$$W_{ij} = \frac{\omega \beta^2 H^2 e^{\hbar/kT}}{32\pi^2 \hbar \rho (e^{\hbar\omega/kT} - 1)} \int \sum_p |G_{ijmn} \langle 1 | S_i | 2 \rangle b_j(\epsilon_{p1} k_m + \epsilon_{pm} k_1)|^2 \frac{d\Omega}{v_{kp}}$$

In the above expression, the various quantities are defined in the following way:

- β : Bohr magneton
- ρ : Crystal density

- G_{ijklm} : Component of spin-lattice interaction tensor
 b_j : Direction cosine of magnetic field direction
 e_{pm} : m^{th} component of phonon polarization unit vector for p^{th} phonon mode
 k_m : m^{th} component of phonon wave vector
 v_{kp} : phonon wave velocity
 $d\Omega$: infinitesimal solid angle containing phonon wave vector.

The undefined quantities have their conventional meaning. In the above expression for the transition probability, the phonon anisotropy is taken into account, although the anisotropy is probably not important in this case. However, computer programs for the evaluation of the transition probability taking anisotropy into account had already been written, and their use added little complication in carrying out the necessary computations.

The results of the computation are shown in Figure 1. In this figure, the angle θ is the angle between the magnetic field and the symmetry axis of the ion under consideration; the angle ϕ represents the azimuth angle above this symmetry axis. It can be seen that there is little dependence of the relaxation time for both ions on the angle ϕ , but that there is a rather strong dependence on the angle θ . The relaxation times are quite long, ranging from 1.5 s to 15 s for Nd^{3+} ions and from 2.1 s to 10 s for U^{3+} ions.

Only very limited measurements have been made on the relaxation time for U^{3+} ions, but their agreement with the calculated value presented here is fair. We have performed a simple saturation measurement at a temperature of $4.2^\circ K$ and a frequency of 9.4 GHz, obtaining an estimated value for the relaxation time of 5 s at $\theta = 90^\circ$ and $\phi = 45^\circ$. This value compares quite well with the computed value of 3.2 s. A more complete measurement has been reported by Berulava, Sanadze, and Khakhanashvili (1965), who observed by means of a pulsed saturation experiment the values $T_1 = 3$ s for $\theta = 0^\circ$ and $T_1 = 0.1$ s for $\theta = 90^\circ$. Although these values are somewhat smaller than those which have been calculated here, the agreement is certainly adequate, in view of the number of simplifying approximations which were made in the calculation.

In the case of Nd^{3+} ions, however, the agreement between experimental and calculated relaxation times is very poor. The relaxation time was measured by Bierig, Weber, and Warshaw (1964) by means of a pulsed saturation experiment. Their result at 4.2° was $T_1 = 2 \times 10^{-4}$ s, in contrast to the calculated value of 8.5 s. This serious disagreement is particularly surprising because of the good agreement in the case of U^{3+} . Both ions have the same electronic configuration and apparently have the same environment, the only deviation from the normal CaF_2 structure being the presence of an interstitial charge-compensating F^- ion. The large disagreement leads, therefore, to the suspicion that some different mechanism than the direct one considered in this calculation may dominate the relaxation process.

One possible mechanism which would lead to a much faster relaxation than that predicted by the theory used here is anomalously large phonon-induced motion of the ions surrounding the magnetic impurity. A localized vibrational mode involving the interstitial F^- ion would be a possibility. It can be shown, however, that such a vibrational mode would lead to ultrasonic resonance absorption much larger than which was observed by Wetsel and Donoho (1965). Furthermore, it is difficult to understand why such a mechanism would not be just as effective in the case of the U^{3+} ions as for the Nd^{3+} ions.

Another possibility would be some mechanism associated with the addition of the Nd impurity to the crystal. Cross relaxation involving some other rapidly relaxing ionic species or even Nd ions in a different symmetry site could lead to a much faster relaxation rate than that calculated here. The postulated rapidly relaxing center would have to exhibit a temperature dependence such that $T_1 = C/T$, however, in order to explain the temperature dependence which has been observed for Nd^{3+} ions. In order to provide an adequate channel for the relaxation of the Nd^{3+} ions the relaxing center would be required to possess a relaxation time several orders of magnitude shorter than that observed for the Nd^{3+} ion unless it were present in a quantity comparable to that of the Nd^{3+} ions. It seems unreasonable, however, to expect to find a magnetic ion which could have such a short relaxation time and

still exhibit the required temperature dependence. At present, therefore, there is no satisfactory theoretical or experimental explanation for the discrepancy between the calculated and experimental relaxation times for Nd^{3+} ion in CaF_2 .

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Figure Caption

Figure 1 Calculated spin-lattice relaxation time for Nd^{3+}
and U^{3+} ions in CaF_2 ; $T = 4.2^\circ\text{K}$, $\nu = 9.4 \text{ GHz}$.

