F. Frazzoli and M. Mancini : A CONTRIBUTION TO THE THEORY
OF SPIN-LATTICE RELAXATION TIME IN RARE-EARTH SALTS.

A Contribution to the Theory
of Spin-Lattice Relaxation Time in Rare-Earth Salts.

F. FRAZZOLI (*)

Laboratori Nazionali del Sincrotrone CNEN - Frascati (Roma)

M. MANCINI

Istituto di Fisica Superiore dell'Università - Firenze

Summary. — A new method for determining the dynamic crystalline field parameters is presented. These parameters are expressed as a function of the effective charge of the diamagnetic molecules surrounding the rare-earth ion. The effective charge is determined from the splitting of the ground state term of the paramagnetic ion in the crystalline field. It is then shown, in the case of neodymium ethylsulphate, that the agreement between the experimental values and the theoretical ones is improved.

Introduction.

A general approach to the theory of spin lattice relaxation time in rare-earth salts has been given by ORBACH [1].

In Orbach's theory the dynamic crystalline field parameters, i.e. the expansion coefficients of the dynamic crystalline potential in series of spherical harmonics, have been assumed approximately to be equal to the static coefficients. However the spin lattice relaxation times evaluated by this method do not agree with the experimental results, in some cases being off by up to three orders of magnitude. In this paper, after having briefly reviewed Orbach's theory (Sect. 1), a method for determining the dynamic crystalline field parameters is presented (Sect. 2). These parameters are expressed as a function

---

(*) Now at the: Istituto di Fisica della Facoltà di Ingegneria - Università di Roma.
[1] R. ORBACH: Proc. Roy. Soc., A 264, 458 (1961).

of the effective charge e' of the diamagnetic molecules surrounding the rare-earth ion. The parameter e' is determined from the splitting of the ground state term of the paramagnetic ion in the crystalline field.

Finally (Sect. 3) it will be shown, in the case of neodymium ethylsulphate, that the discrepancy between the experimental values and the theoretical ones evaluated according to Orbach's procedure is greatly reduced when the new approach is used.

1. – Resume of Orbach's theory.

For rare earth ions in crystals we take a Hamiltonian $\mathscr{H} = \mathscr{H}_{so} + \mathscr{H}_c + \mathscr{H}_z$, the terms representing the spin-orbit, crystal field and Zeeman interactions, respectively.

The spin-orbit splitting ($\sim 10^3$ cm^{-1}) is considerably greater than the crystal field splittings Δ_1, Δ_2 ... ($\sim 10^2$ cm^{-1}) (Fig. 1), so that the lowest J multiplet of the free ion i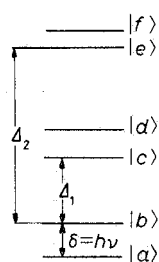s split by the crystal field into a manifold of states, each of which may be approximately represented by a suitable linear combination of the basis wave function $|JJ_z\rangle$. For ions with an odd number of electrons each state is at least twofold degenerate. This degeneracy may be removed by an external magnetic field H, resulting in a series of doublets $|a\rangle$ and $|b\rangle$, $|c\rangle$ and $|d\rangle$, etc. For ions with an even number of electrons, some of the states may be singlets but we assume that a magnetic doublet lies lowest (this situation is often verified).

Fig. 1. – Schematic energy level diagram of the lowest state of a rare-earth ion in a crystalline field (splittings Δ_1, Δ_2, ...) and in a magnetic field (splitting δ).

The spin-lattice interaction operator couples the spin system to the lattice in such a way that spin-system transitions may occur $|b\rangle \leftrightarrow |a\rangle$ and the lattice may absorb the energy difference. The dominant mechanism for such transitions, as was suggested by HEITLER and TELLER [2], FIERZ [3], KRONIG [4] and VAN VLECK [5], is the modulation of the electrostatic crystalline field by lattice vibrations. The crystalline electric field, arising from the effect of the charges of the neighbouring diamagnetic ions and molecules on the paramagnetic ion, is modulated by the lattice vibrations which distort the distributions of charges. These distorsions are proportional to the averaged strain ε of the lattice [1].

---

[2] W. HEITLER and E. TELLER: Proc. Roy. Soc., A 155, 629 (1936).

[3] M. FIERZ: Physica, 5, 433 (1938).

[4] R. DE L. KRONIG: Physica, 6, 33 (1939).

[5] J. H. VAN VLECK: Phys. Rev., 57, 426 (1940).

As ε is small at temperatures much less than the melting point of the material it may be used as an expansion parameter for the crystalline potential in which the magnetic electrons move. We will have

$$(1.1) \qquad V = V^{(0)} + V^{(1)}\varepsilon ,$$

where higher-order terms in ε have been neglected. The first term on the right is just the static term which, together with the spin-orbit coupling and the Zeeman interaction generates our eigenstates $|a\rangle$, $|b\rangle$ .... The second term is the spin-lattice interaction which we shall consider and is clearly just the first-order dynamic part of the electric potential in which the magnetic electrons move.

It is useful to expand V into a series of terms

$$(1.2) \qquad V = \sum_{l,m} A_l^m r^l Y_l^m(\theta, \varphi) ,$$

where r denotes the radius of the $4f$ electron concerned, Y_l^m the spherical harmonic of degree l and azimuthal quantum number m, A_l^m a crystalline field parameter, which depends on the charges and on the positions of the surrounding molecules, hence we shall have

$$(1.3) \qquad V^{(0)} = \sum_{l,m} A_l^m(0) r^l Y_l^m(\theta, \varphi) ,$$

$$(1.4) \qquad V^{(1)} = \sum_{l,m} \left(\frac{\partial A^m}{\partial \varepsilon}\right)_{\varepsilon=0} r^l Y_l^m(\theta, \varphi) .$$

The expansion (1.4) for the dynamic crystalline potential is very useful because one can make use of all the formal simplifications first elaborated by STEVENS ([6-9]) in calculating the matrix elements of the static crystalline electric field between spin Hamiltonian states.

For the spin-lattice relaxation time τ one has ([1,10])

$$(1.5) \qquad \frac{1}{\tau} = 3\frac{(\delta_{ab})^2 KT}{\pi\varrho v^5 \hbar^4} |\langle a|V|b\rangle|^2 +$$

$$+ \frac{9}{16\pi^3 \varrho^2 v^{10}} \int_0^{2\pi\nu_D} \left| \sum_l \frac{\langle a|V_1|l\rangle\langle l|V_1|b\rangle}{\hbar\omega' - \Delta_l} \right|^2 \text{cosech}^2 \frac{\hbar\omega'}{2KT} \omega'^6 \, d\omega'$$

[6] R. J. ELLIOTT and K. W. H. STEVENS: *Proc. Roy. Soc.*, A **215**, 437 (1952).
[7] R. J. ELLIOTT and K. W. H. STEVENS: *Proc. Roy. Soc.*, A **218**, 553 (1953).
[8] R. J. ELLIOTT and K. W. H. STEVENS: *Proc. Roy. Soc.*, A **219**, 387 (1953).
[9] K. W. H. STEVENS: *Proc. Phys. Soc.*, A **65**, 209 (1952).
[10] R. BRUZZESE, F. FRAZZOLI, M. MANCINI, G. SACERDOTI, G. TORALDO DI FRANCIA and F. UCCELLI: INFN/FM-65/3 (1965).

where the symbols are defined in ref. ([10]). There are some difficulties about the dynamic crystalline coefficients

$$\left(\frac{\partial A_l^m}{\partial \varepsilon}\right)_{\varepsilon=0},$$

for they are unknown, while the static ones $A_l^m(0)$ are often known from magnetic resonance and optical experiments ([8]).

In Orbach's theory the crystalline field parameters $(\partial A_l^m/\partial \varepsilon)_{\varepsilon=0}$ have been assumed approximately to be equal to the static coefficients $A_l^m(0)$. In particular Orbach sets

(1.6) $$\left(\frac{\partial A_l^m}{\partial \varepsilon}\right)_{\varepsilon=0} \langle r^l \rangle = |A_l^0(0) \langle r^l \rangle|,$$

when $l = 2,\ 4$ and

(1.7) $$\left(\frac{\partial A_6^m}{\partial \varepsilon}\right)_{\varepsilon=0} \langle r^6 \rangle = \left[|A_6^0(0) r^6|^{6-|m|} |A_6^6(0) \langle r^6 \rangle|^m\right]^{\frac{1}{6}},$$

where $\langle r^l \rangle$ denotes the mean of the l-th power of r.

This approach was based on his satisfactory calculations of phonon anharmonic coefficients in dielectric crystals, though its extension to the present case, as ORBACH himself has remarked, must be regarded as a very rough approximation.

2. – Evaluation of the dynamic crystalline field parameters.

We shall limit ourselves to considering compounds in which the crystalline electric field at the paramagnetic ion site is due to molecules of the same kind, though this limitation may be easily removed.

In order to give a concrete example we shall consider the case of rare earth ethylsulphates. The geometrical configuration of the nearest neighbour molecules about the paramagnetic ion is shown in Fig. 2. In these compounds each rare-earth ion is surrounded by nine water molecules of hydration and three ethyl radicals.
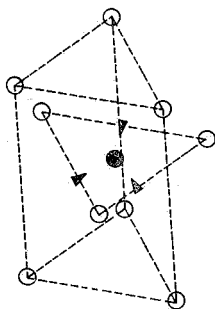

Fig. 2. – A perspective drawing (not to scale) of the configuration surrounding the trivalent rare-earth ion in the ethyl sulphate. Only the nearest neighbour molecules are drawn in for simplicity. o water molecule, ● rare-earth ion, ▲ ethyl radical.

The crystalline electric field at the site of the rare earth ion is mainly due to the nine neighbouring water molecules [11]. Following the point-charge model [12] as far as the evaluation of the crystalline field is concerned, the nine water molecules surrounding the rare-earth ion will be replaced by nine point charges e'. Accordingly the electric potential $V(r, \theta, \varphi)$ due to the surrounding point charges, at a point (r, θ, φ) near the origin at the magnetic ion in question is

$$(2.1) \qquad V(r, \theta, \varphi) = e' \sum_{j=1}^{9} \frac{1}{|\boldsymbol{R}_j - \boldsymbol{r}|}$$

where $\boldsymbol{R}_j \equiv (R_j, \theta_j, \Phi_j)$ denotes the distance of the point charge pertinent to the j-th water molecule.

An alternative method of expressing V is to write it directly in spherical harmonics. From ref. [12] one has

$$(2.2) \qquad V(r, \theta, \varphi) = \sum_n \sum_{m=-n}^{+n} r^n A_n'^m Y_n^m(\theta, \varphi),$$

where

$$(2.3) \qquad A_n'^m r^n = e' \sum_{j=1}^{9} \frac{4\pi}{(n+1)} \frac{r^n}{R_j^{n+1}} (-1)^m Y_n^{-m}(\theta_j, \Phi_j).$$
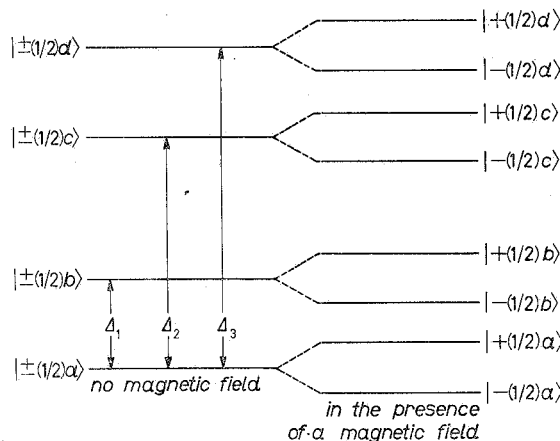
Fig. 3. – A hypothetical level diagram for a Kramers salt in a field of trigonal symmetry. In the absence of a magnetic field each level is doubly degenerate (left side of the Figure) $p, q, r, \ldots$ being odd integers. The splittings on the right side of the Figure represent the level structure in the presence of a magnetic field.

[11] J. DWECK and G. SEIDEL: Phys. Rev., 151, 290 (1966).
[12] H. T. HUTCHINGS: Solid State Physics, vol. 16 (1964).

1307

In the case of ethylsulphates the neighbourhood of a rare-earth ion produces a field of trigonal symmetry ([13]). Therefore the energy levels of ions containing an odd number of electrons are split by the crystalline field into $J+\frac{1}{2}$ doublets, where J is the quantum number referring to the total angular momentum. When the number of electrons is even we obtain singlets and doublets. Let us consider the case of Kramers salts and let $|\pm\frac{1}{2}a\rangle$; $|\pm\frac{1}{2}b\rangle$; $|\pm\frac{1}{2}c\rangle$ etc. denote the doublets in which the ground state term is split by the crystalline field and let Δ_1, Δ_2, etc. be the relative energy splittings (Fig. 3).

Denoting by $\mathcal{H}_{cr}$ the energy of electrons of the unfilled shell in the electric field of the crystal $\left[\mathcal{H}_{cr} = -\sum_i eV(r_i,\,\theta_i,\,\Phi_i)\right.$, where r_i, θ_i, Φ_i are the co-ordinates of the i-th electron of the unfilled shell and e denotes the electronic charge$\big]$ from standard perturbation theory ([14]) one has

$$(2.4) \quad \begin{cases} \Delta_1 = \langle\tfrac{1}{2}\,b|\mathcal{H}_{cr}|\tfrac{1}{2}\,b\rangle - \langle\tfrac{1}{2}a|\mathcal{H}_{cr}|\tfrac{1}{2}a\rangle\,, \\[2mm] \Delta_2 = \langle\tfrac{1}{2}\,c|\mathcal{H}_{cr}|\tfrac{1}{2}\,c\rangle - \langle\tfrac{1}{2}a|\mathcal{H}_{cr}|\tfrac{1}{2}a\rangle\,, \\[2mm] \Delta_3 = \langle\tfrac{1}{2}d|\mathcal{H}_{cr}|\tfrac{1}{2}d\rangle - \langle\tfrac{1}{2}a|\mathcal{H}_{cr}|\tfrac{1}{2}a\rangle\,, \\[2mm] \Delta_4 = \langle\tfrac{1}{2}\,e|\mathcal{H}_{cr}|\tfrac{1}{2}\,e\rangle - \langle\tfrac{1}{2}a|\mathcal{H}_{cr}|\tfrac{1}{2}a\rangle\,. \end{cases}$$

The energy splittings Δ_1, Δ_2 etc. and also the explicit form of the eigenfunctions of the doublets $|\pm\frac{1}{2}a\rangle$; $|\pm\frac{1}{2}b\rangle$, etc. can be derived from experiment ([6]). Expressing in (2.4) the crystalline field potential according to the point charge model, eq. (2.2), successively eqs. (2.4) can be used to obtain an estimate of e' by means of a best fitting procedure.

Let us now suppose that the evaluation of e' has been carried out. Then if in eq. (2.1) R_j is varied by an arbitrarily oriented vector ΔR_j, where $|\Delta R_j| = \Delta R$ is of the order of magnitude of molecular oscillations, the new potential $V' = V + \Delta V$ will be

$$(2.5) \qquad V' = V + \Delta V = e'\sum_{j=1}^{9}\frac{1}{|R_j + \Delta R_j - r|}\,.$$

In the static case, due to symmetry restrictions, only the coefficients A_2^0, A_4^0, A_6^0, A_6^6 in the expansion of V in a series of spherical harmonics, must be retained ([1]). In the expansion of V': $V' = \sum_{l,m} A_l'^m r^l Y_l^m(\theta,\varphi)$, from the reduction in symmetry due to the molecular oscillations, it turns out ([1]) that all the coefficients A_m' are in general different from zero. Hence this same property will hold for the coefficients ΔA_l^m related to the expansion of ΔV in terms

---

([13]) W. Low: *Solid State Physics*, vol. 2 (1960).

([14]) P. Fong: *Elementary Quantum Mechanics* (London, 1962).

of spherical harmonics

$$(2.6) \qquad \Delta V = e' \sum_{j=1}^{9} \left(\frac{1}{|\boldsymbol{R}_j + \Delta \boldsymbol{R}_j - \boldsymbol{r}|} - \frac{1}{|\boldsymbol{R}_j - \boldsymbol{r}|} \right) = \sum_{l,m} \Delta A_l^m r^l Y_l^m(\theta, \varphi).$$

As far as the evaluation of the spin-lattice relaxation time is concerned only the coefficients ΔA_l^m, with $l = 2, 4, 6$; $(-l \leqslant m \leqslant l)$ have to be known [1] Moreover the presence of the factor r^l leads reasonably to a rapid convergence of the series (2.6) so that we can limit the expansion (2.6) to the spherical harmonics of degree $l = 6$.

The set of 28 unknown coefficients $\Delta A_l^m [\Delta A_l^m = (\Delta A_l^{-m})^*$ since ΔV is real] is then obtained by solving the system (2.7) with a computer:

$$(2.7) \qquad \Delta V(P_i) = \sum_{l,m} A_l^m (r^l Y_l^m)_{P_i}, \qquad i = 1, 2, \dots, 28, \quad -l \leqslant m \leqslant l,$$

where the quantities $\Delta V(P_i)$ and $(r^l Y_l^m)_{P_i}$ are evaluated at 28 points P_i arbitrarily chosen in the region of maximum probability for the $4f$ electrons.

In order to establish the connection between the coefficients ΔA_l^m and the parameters

$$\left(\frac{\partial A_l^m}{\partial \varepsilon} \right)_{\varepsilon=0},$$

we note that from ref. [15] one has

$$(2.8) \qquad A_l^m = A_l^m(0) + \varepsilon R \left(\frac{\Delta A_l^m}{\Delta R} \right) + \text{higher-order terms in } \varepsilon,$$

where R is the average distance of the water molecules from the origin $[R \simeq 2.5 \text{ Å}$ in the case of ethylsulphates [16]].

From the identity

$$(2.9) \qquad \left(\frac{\Delta A_l^m}{\Delta R} \right) \varepsilon \cdot R = \varepsilon \left(\frac{\partial A_l^m}{\partial \varepsilon} \right)_{\varepsilon=0},$$

one easily obtains

$$(2.10) \qquad \left(\frac{\partial A_l^m}{\partial \varepsilon} \right)_{\varepsilon=0} = \left(\frac{\Delta A_l^m}{\Delta R} \right) R.$$

Note that for our purposes it is not necessary to know the exact values of ΔR, for we are interested in evaluating $\Delta A_l^m / \Delta R$ which is practically independent

[15] P. L. SCOTT and C. D. JEFFRIES: Phys. Rev., 127, 32 (1962).

[16] J. A. A. KETELAAR: Physica, 4, 619 (1937).

of R since the relation $\Delta R \ll |R_j|$ is always satisfied. The order of magnitude of ΔR has been evaluated by means of the method outlined in ref. [17]. The order of magnitude of ΔR at $\simeq 4$ °K turns out to be $\simeq 0.01$ Å.

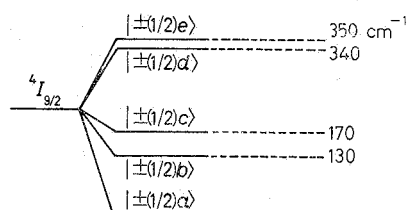## 3. – Spin-lattice relaxation time in neodymium ethylsulphate.

Fig. 4. – A schematic energy-level diagram for Nd³⁺ in ethyl sulphate (not to scale).

The free Nd⁺⁺⁺ ion ground level $4f^3$, $^4I_{9/2}$ is split by the ethylsulphate crystal field into five doublets. From ref. [8] the energy states and levels are as collected in Table I.

A schematic distribution of the energy levels is shown in Fig. 4.

Expressing the potential of the crystalline field according to the point-charge

TABLE I. – *The g values, splitting, and wave functions for neodymium ethylsulphate.*

Wave function	Zero field splitting (cm⁻¹)	$g_\parallel$	$g_\perp$
$\vert \pm \tfrac{1}{2}a \rangle = 0.92\vert \pm \tfrac{7}{2} \rangle + 0.38\vert \pm \tfrac{5}{2} \rangle$	0	3.56	2.12
$\vert \pm \tfrac{1}{2}b \rangle = \vert \pm \tfrac{1}{2} \rangle$	130	0.73	3.64
$\vert \pm \tfrac{1}{2}c \rangle = 0.75\vert \pm \tfrac{9}{2} \rangle + 0.66\vert \mp \tfrac{3}{2} \rangle$	170	2.73	0
$\vert \pm \tfrac{1}{2}d \rangle = 0.38\vert \pm \tfrac{7}{2} \rangle - 0.92\vert \mp \tfrac{5}{2} \rangle$	340	2.34	2.03
$\vert \pm \tfrac{1}{2}e \rangle = 0.66\vert \pm \tfrac{9}{2} \rangle - 0.75\vert \mp \tfrac{3}{2} \rangle$	350	1.62	0

model, then eqs. (2.4) in the case of neodymium-ethylsulphate assume the form

$$\Delta_1 = 130 \text{ cm}^{-1} = \langle 1/2 | K_2^0 Y_2^0 + K_4^0 Y_4^0 + K_6^0 Y_6^0 | 1/2 \rangle - \Delta,$$

$$\Delta_2 = 170 \text{ cm}^{-1} = 0.56 \langle 9/2 | K_2^0 Y_2^0 + K_4^0 Y_4^0 + K_6^0 Y_6^0 | 9/2 \rangle +$$

$$+ 0.49 \langle 9/2 | K_6^6 Y_6^{-6} | -3/2 \rangle + \langle -3/2 | K_6^6 Y_6^{-6} | 9/2 \rangle +$$

$$+ 0.43 \langle -3/2 | K_2^0 Y_2^0 + K_4^0 Y_4^0 + K_6^0 Y_6^0 | -3/2 \rangle - \Delta,$$

$$\Delta_3 = 340 \text{ cm}^{-1} = 0.14 \langle 7/2 | K_2^0 Y_2^0 + K_4^0 Y_4^0 + K_6^0 Y_6^0 | 7/2 \rangle - \Delta,$$

[17] A. ABRAGAM: *L'effet Mössbauer* (Paris, 1964).

$$\Delta_4 = 350 \text{ cm}^{-1} = 0.43\langle 9/2|K_2^0 Y_2^0 + K_4^0 Y_4^0 + K_6^0 Y_6^0|9/2\rangle -$$

$$- 0.49\langle 9/2|K_6^6 Y_6^{-6}|-3/2\rangle + \langle -3/2|K_6^6 Y_6^6|9/2\rangle +$$

$$+ 0.56\langle 3/2|K_2^0 Y_2^0 + K_4^0 Y_4^0 + K_6^0 Y_6^0|3/2\rangle - \Delta \,,$$

where

$$\Delta = 0.84\langle 7/2|K_2^0 Y_2^0 + K_4^0 Y_4^0 + K_6^0 Y_6^0|7/2\rangle +$$

$$+ 0.35\langle 7/2|K_6^6 Y_6^{-6}|-5/2\rangle + \langle -5/2|K_6^6 Y_6^6|7/2\rangle +$$

$$+ 0.14\langle -5/2|K_2^0 Y_2^0 + K_4^0 Y_4^0 + K_6^0 Y_6^0|-5/2\rangle$$

and

$$K_l^m = - 3eA_l^m \langle r^l\rangle \,.$$

From ref. [18] one has

$$\langle r^2\rangle = 0.279 \text{ Å}^2 \,,$$

$$\langle r^4\rangle = 0.188 \text{ Å}^4 \,,$$

$$\langle r^6\rangle = 0.163 \text{ Å}^6 \,.$$

The evaluation of the matrix elements appearing in (3.1) has been carried out by the equivalent operator method ([9]).

Assuming the vectors R_j approximately to be equal to the position vectors of the water molecules which are reported in ref. ([16]) one finds that eqs. (3.1) are fitted by $e' = 0.01e$.

It must be remembered that in the iron group the effective charge of water molecules turned out of the same order of magnitude of the electronic charge ([5,19]). This is coherent with our results as in the rare-earth salts the crystalline field splittings are about two orders of magnitude smaller than those of iron group salts. Using the value so obtained for e' we have solved the system (2.6). The solutions ΔA_l^m along with the corresponding values of $(\partial A_l^m/\partial \varepsilon)_{\varepsilon=0}$ are collected in Table II.

We have then verified that the expression

(3.3) $$\sum_{l,m}^{6} A_l^m r^l Y_l^m$$

reproduces to a good approximation (at least 5%) the effective variation ΔV of the crystalline potential in the region where $4f$ wave functions are meaningfully different from zero.

([18]) A. J. FREEMAN and R. E. WATSON: *Phys. Rev.*, **127**, 2058 (1962).

([19]) J. H. VAN VLECK: *Journ. Chem. Phys.*, **7**, 72 (1939).

TABLE II. - *Solution of the system* (2.7) *along with the required values of* $(\partial A_l^m/\partial \varepsilon)_{\varepsilon=0}$.

ΔA_l^m (erg cm^{-l})	$\left(\dfrac{\partial A_l^m}{\partial \varepsilon}\right)_{\varepsilon=0}$ (ryd cm^{-l}) (l, m)	ΔA_l^m (erg cm^{-l})	$\left(\dfrac{\partial A_l^m}{\partial \varepsilon}\right)_{\varepsilon=0}$ (ryd cm^{-l}) (l, m)
$\Delta A_0^0 = -2.371 \cdot 10^{-14}$		$\Delta A_4^4 = -1.175 \cdot 10^{-13}$	$(4, 4) = -1.468 \cdot 10^4$
$\Delta A_1^0 = 6.785 \cdot 10^{-15}$		$\Delta A_5^0 = -2.785 \cdot 10^{-15}$	
$\Delta A_1^1 = -2.785 \cdot 10^{-14}$		$\Delta A_5^1 = -2.652 \cdot 10^{-14}$	
$\Delta A_2^0 = 1.581 \cdot 10^{-13}$	$(2, 0) = 1.976 \cdot 10^4$	$\Delta A_5^2 = 1.418 \cdot 10^{-13}$	
$\Delta A_2^1 = -6.19 \cdot 10^{-16}$	$(2, 1) = 7.735 \cdot 10^3$	$\Delta A_5^3 = 6.755 \cdot 10^{-14}$	
$\Delta A_2^2 = 1.266 \cdot 10^{-13}$	$(2, 2) = 1.583 \cdot 10^4$	$\Delta A_5^4 = -3.124 \cdot 10^{-15}$	
$\Delta A_3^0 = 5.87 \cdot 10^{-15}$		$\Delta A_5^5 = 1.110 \cdot 10^{-13}$	
$\Delta A_3^1 = 5.025 \cdot 10^{-14}$		$\Delta A_6^0 = -1.522 \cdot 10^{-14}$	$(6, 0) = -1.902 \cdot 10^3$
$\Delta A_3^2 = -2.176 \cdot 10^{-14}$		$\Delta A_6^1 = 1.117 \cdot 10^{-12}$	$(6, 1) = 1.396 \cdot 10^3$
$\Delta A_3^3 = -4.895 \cdot 10^{-14}$		$\Delta A_6^2 = -2.269 \cdot 10^{-17}$	$(6, 2) = -2.836$
$\Delta A_4^0 = 2.817 \cdot 10^{-14}$	$(4, 0) = 3.522 \cdot 10^3$	$\Delta A_6^3 = -3.218 \cdot 10^{-14}$	$(6, 3) = -4.022 \cdot 10^3$
$\Delta A_4^1 = 1.088 \cdot 10^{-13}$	$(4, 1) = 1.361 \cdot 10^4$	$\Delta A_6^4 = 9.875 \cdot 10^{-15}$	$(6, 4) = 1.234 \cdot 10^3$
$\Delta A_4^2 = 3.395 \cdot 10^{-14}$	$(4, 2) = 4.244 \cdot 10^3$	$\Delta A_6^5 = -4.73 \cdot 10^{-14}$	$(6, 5) = -5.9 \cdot 10^3$
$\Delta A_4^3 = 4.222 \cdot 10^{-14}$	$(4, 3) = -5.280 \cdot 10^3$	$\Delta A_6^6 = -4.79 \cdot 10^{-14}$	$(6, 6) = -5.99 \cdot 10^3$

With a magnetic field H, which we shall suppose to be parallel to the symmetry axis of the crystal, the first-order corrected wave functions of the lowest doublet are

$$(3.4) \quad \begin{cases} |b\rangle = |-\tfrac{1}{2}a\rangle + \beta H \Lambda \left(\dfrac{\langle \tfrac{1}{2}d|J_z|\tfrac{1}{2}a\rangle}{\Delta_d} |\tfrac{1}{2}d\rangle \right), \\ |a\rangle = |\tfrac{1}{2}a\rangle + \beta H \Lambda \left(\dfrac{\langle -\tfrac{1}{2}d|J_z|-\tfrac{1}{2}a\rangle}{\Delta_d} |-\tfrac{1}{2}d\rangle \right), \end{cases}$$

where the symbols are defined in ref. ([1,10]).

Making use of (3.4) we can easily show that the expression (1.5) of the spin lattice relaxation time as a function of the magnetic field and of the tem-

perature turns out to be

(3.5)
$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2},$$

where

(3.6) $$\frac{1}{\tau_1} = \frac{12\beta^4 g_{\parallel}^2 \Lambda^2}{\pi \varrho v^5 h^4 \Delta_d^2} |\langle \tfrac{1}{2}d|J_z|\tfrac{1}{2}a\rangle|^2 \, |\langle -\tfrac{1}{2}d| \sum_{l,m} \left(\frac{\partial A_l^m}{\partial \varepsilon}\right)_{\varepsilon=0} \langle r^l\rangle \, Y_l^m|\tfrac{1}{2}a\rangle|^2 H^4 T,$$

(3.7) $$\frac{1}{\tau_2} = \frac{9!\hbar^2}{4\pi^3 \varrho^2 v^{10}} \cdot$$

$$\cdot \left(\frac{K}{\hbar}\right)^9 \sum_k \frac{|\langle -\tfrac{1}{2}a| \sum_{l,m} (\partial A_l^m/\partial\varepsilon)_{\varepsilon=0}\langle r^l\rangle \, Y_l^m|\tfrac{1}{2}k\rangle \langle \tfrac{1}{2}k| \sum_{lm} (A^m/\partial\varepsilon)_{\varepsilon=0}\langle r^l\rangle \, Y_l^m|\tfrac{1}{2}a\rangle|^2}{\Delta_k^4} T^9 .$$

Let us first evaluate $1/\tau_1$. We have

$$\langle \tfrac{1}{2}d|J_z|\tfrac{1}{2}a\rangle = [\, 0.38\langle 7/2| - 0.92\langle -5/2|\,]\, J_z[\, 0.92|7/2\rangle + 0.38|-5/2\rangle\,] = 2.09 .$$

Hence

$$\langle \tfrac{1}{2}d|J_z|a\rangle^2 = 4.368 .$$

It turns out that the largest contribution to

$$\langle -\tfrac{1}{2}d| \sum_{l,m} \left(\frac{\partial A_l^m}{\partial\varepsilon}\right)_{\varepsilon=0} \langle r^l\rangle \, Y_l^m|\tfrac{1}{2}a\rangle$$

comes from matrix elements for $n = 6$. We find

$$\left|\langle -\tfrac{1}{2}d| \sum_{l,m} \left(\frac{\partial A_l^m}{\partial\varepsilon}\right)_{\varepsilon=0} \langle r^l\rangle \, Y_l^m|\tfrac{1}{2}a\rangle\right|^2 \simeq 3.05 \cdot 10^5 .$$

Making use of the following values of the constants $\varrho = 1.7$ g/cm^3, $\Lambda = 8/11$, $v = 2.5 \cdot 10^5$ cm/s the spin-lattice relaxation time due to direct processes in neodymium ethylsulphate is

$$\frac{1}{\tau_1} = 3.506 \cdot 10^{-14} H^4 T \, \text{s}^{-1},$$

where H is in oersted.

In evaluating $1/\tau_2$, we will consider as intermediate states only the doublets $|\pm\tfrac{1}{2}b\rangle$, $|\pm\tfrac{1}{2}c\rangle$, and ignore contributions from higher levels by virtue of the energy denominators in (3.7). Then one finds

$$\frac{1}{\tau_2} = 2.095 \cdot 10^{-1} T^9 \, \text{s}^{-1}.$$

TABLE III. – *Comparison of measured data and theoretical estimates of the spin-lattice relaxation time for neodynium ethylsulphate.*

T °K	(Gauss)	τ^{-1} (meas.) in s^{-1}	τ^{-1} (Orbach's procedure) in s^{-1}	τ^{-1} (point-charge model) in s^{-1}
1.380	780	5.43	9.42	3.82
1.380	1030	5.10	21.95	3.85
1.380	1290	4.81	52.58	3.93
1.380	1540	5.88	105.78	4.07
1.380	1790	6.13	192.25	4.29
1.380	2040	7.94	323.64	4.64
1.380	2290	8.26	513.33	5.13
1.380	2540	8.00	776.43	5.81
1.592	780	7.75	11.56	13.7
1.592	1030	7.66	27.79	13.8
1.592	1290	6.49	63.12	13.9
1.592	1540	6.94	124.49	14
1.592	1790	7.09	224.25	14.3
1.592	2040	8.26	375.83	14.7
1.592	2290	8.97	594.65	15.2
1.592	2540	8.62	898.177	16
1.685	780	8.62	14.44	22.9
1.685	1030	5.68	31.6	23
1.685	1290	6.29	69.01	23.1
1.685	1540	6.94	133.96	23.2
1.685	1790	6.45	239.55	23.5
1.685	2060	6.62	399.98	24
1.685	2290	8.55	631.59	24.5
1.685	2540	9.26	1030	25.3
1.875	780	17.59	25.12	60
1.875	1030	14.93	44.23	60
1.875	1290	13.33	85.84	60.1
1.875	1540	14.70	158.12	60.3
1.875	1790	14.93	375.611	60.6
1.875	2040	14.70	454.13	61.1
1.675	2290	15.62	711.86	61.8
1.875	2540	15.38	1069.33	62.7
2.06	1030	16.67	69.04	140
2.06	1290	13.89	116.24	140.1
2.06	1540	13.70	198.22	140.3
2.06	1790	14.92	331.48	140.6
2.06	2040	15.38	533.96	141.2
2.06	2290	15.87	826.28	141.9
2.06	2540	16.39	1231.74	142.9
4.22	1030	90.91	$23.4 \cdot 10^3$	$88.9 \cdot 10^3$
4.22	1290	90.91	$23.5 \cdot 10^3$	$88.9 \cdot 10^3$
4.22	1540	76.92	$23.66 \cdot 10^3$	$88.9 \cdot 10^3$
4.22	1790	67.50	$23.92 \cdot 10^3$	$88.9 \cdot 10^3$

Hence the expression of the spin-lattice relaxation time in the case of neodymium ethylsulphate turns out to be

$$\frac{1}{\tau} = 3.506 \cdot 10^{-14} H^4 T + 2.095 \cdot 10^{-1} T^9 \ \mathrm{s}^{-1},$$

while using Orbach's hypotheses [10] one obtains

$$\frac{1}{\tau} = 135.1 \cdot 10^{-18} H^4 T + 0.055 T^9 \ \mathrm{s}^{-1}.$$

The theoretical estimates along with the experimental data due to RIECKOFF, WESEMEYER and DANIELS [20,21] are collected in Table III.

4. – Conclusions.

It can be easily seen that in the ranges of temperature T and magnetic field H experimentally studied, the behaviour of the relaxation time as a function of H and T agrees reasonably well with the theoretical predictions based upon the point-charge model, while the relaxation time from Orbach's hypothesis exhibits a much too strong dependence on H. Our numerical estimates agree reasonably well with the experimental values up to about 2 °K.

We would like to make some remarks about the approach we have used. By assuming that the field from the water molecules is similar to that of point charges we have neglected the finite size of the water molecules. A better approximation would be to treat the water molecules as dipoles rather than as charges. Nevertheless in the dipole approximation one could deal with the delicate question of just how much the dipole turns during the motion and this would lead to excessive mathematical difficulties. On the other hand VAN VLECK has shown in the case of iron-group salts [19] that the point charge and dipole approximations do not differ too greatly.

Furthermore we have neglected the direct effect of the « distant » charges i.e. the molecules more remote than the nine water molecules immediately surrounding the paramagnetic ion, however, since in this method the effective charge of the water molecules is obtained from the splitting of the ground state $^4I_{9/2}$ of the Nd^{+++} in the crystalline field, the effect of the distant molecules is taken into account indirectly.

Moreover in the point-charge model the overlapping of the magnetic-ion wave function with those of neighbouring atoms has been neglected. But as the magnetic properties of rare-earth ions are due to the low $4f$ electrons,

[20] H. WESEMEYER and J. DANIELS: Zeits. f. Phys., 152, 5 (1958).

[21] J. M. DANIELS and K. E. RIECKHOFF: Canad. Journ. Phys., 38, 604 (1960).

whose mean distance from the nucleus is much less than for $3d$ electrons, the point-charge model seems to be more appropriate for the rare-earth case than for the iron-group salts.

Finally we note that we have assumed the position vectors R_j of the point charges to be equal to those of the corresponding molecules. These in turn have been determined by X-ray methods ([16]) and hence they actually refer to the oxygens. Hence a better approximation should be introduced by considering the positions vector R_j, together with the effective charge l', as parameters to be determined by the best fit with the experimental results. Here we have neglected this refinement as our purpose was only to outline the advantage of the present approach.

<div align="center">* * *</div>

The authors are greatly indebted to Prof. G. TORALDO DI FRANCIA and G. C. SACERDOTI for helpful discussions and criticism and to Dr. Eng. F. UC-CELLI for is help in the computational work.

<hr>

<div align="center">RIASSUNTO</div>

Viene presentato un nuovo metodo per determinare i coefficienti dello sviluppo, in serie di armoniche sferiche, del campo cristallino dinamico. Questi coefficienti, da cui dipende il tempo di rilassamento, vengono espressi in funzione della carica efficace delle molecole che circondano lo ione paramagnetico in esame. La carica efficace è determinata dalla separazione del termine fondamentale dello ione nel campo cristallino. Si fa poi vedere che con il nuovo metodo si ottiene un migliore accordo con i dati sperimentali.

<div align="center">**Вклад в теорию спин-решеточного времени релаксации
в солях редкоземельных элементов.**</div>

Резюме (*). — Предлагается новый метод для определения параметров динамического кристаллического поля. Эти параметры выражаются как функция эффективного заряда диамагнитных молекул, окружающих редкоземельный ион. Эффективный заряд определяется из расщепления терма основного состояния парамагнитного иона в кристаллическом поле. Затем показывается, что в случае этилсульфата неодима согласие между экспериментальнымии теоретическими величинами улучшается.

<hr>

(*) *Переведено редакцией.*