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HAL Id: jpa-00209576
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Submitted on 1 Jan 1983

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Electron spin-lattice relaxation in a true amorphous material : V⁴⁺ in V₂O₅

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(Reçu le 16 février 1982, révisé le 6 septembre, accepté le 10 septembre 1982)

Résumé. — Nous avons mesuré le temps de relaxation spin électronique-réseau $T_1$ de l’ion V⁴⁺ dans V₂O₅ en bande X entre 1,4 et 100 K : $T_1^{-1} = 39 T^2 \int_0^{56/T} \frac{x \, dx}{\sinh x}$. Nous expliquons ce comportement à l’aide d’un processus faisant intervenir la modulation du champ cristallin par un S.D.N., et un phonon. On doit associer la température caractéristique de 56 K non pas au maximum de l’énergie des S.D.N., mais à l’énergie de coupure dans la distribution du paramètre d’asymétrie $\delta$. La relaxation spin-réseau se montre ainsi capable de fournir des informations sur l’asymétrie.

Abstract. — The electron spin-lattice relaxation time $T_1$ of V⁴⁺ in amorphous V₂O₅ has been measured in the X-band between 1.4 K and 100 K : $T_1^{-1} = 39 T^2 \int_0^{56/T} \frac{x \, dx}{\sinh x}$. We explain this behaviour using a process requiring one two-level system (T.L.S.) modulating the crystal field, and one phonon. The characteristic temperature 56 K must be associated not with the maximum energy of the T.L.S. but with the cut-off in the distribution of the asymmetry parameter $\delta$. Spin-lattice relaxation is thus able to give informations about the asymmetry.

1. Introduction. — Since Zeller and Pohl’s first experiments [1], a number of works have established that amorphous materials possess physical properties strikingly different from those of crystalline solids. Below 1 K the specific heat $C_V$ and thermal conductivity $\kappa$ do not display the usual cubic temperature dependence, but obey a nearly linear and quadratic law respectively. These properties have been interpreted independently by Anderson, Halperin, Varma [2] and by Phillips [3]. Their model postulates the existence of a large number of « tunnelling systems », presumably atoms or groups of atoms undergoing quantum tunnelling between two minima of the potential energy; it is argued that at the low temperatures of interest only the two lowest levels of each tunnelling system need be considered, and this leads to the two-level system (T.L.S.) concept. A $C_V \propto T$ law is then easily established by assuming that the density of states for these T.L.S. is nearly constant from $E \sim 0$ up to an energy $E_M$ of about 0.1 eV. The low $\kappa$ value and its $T^2$ dependence are explained by assuming that T.L.S. do not carry energy, but are strongly coupled to the phonons and are thus able to scatter them. A success of this model was the theoretical prediction of the saturation of the ultrasonic absorption, effectively observed later [3, 4]. However, a more detailed knowledge of the microscopic nature of these T.L.S. is still lacking. It seems reasonable to think that experimental methods using microscopic probes, like E.S.R., could provide information of interest. In order to get such information one must first choose an amorphous material with electron spins (not to be confused with the « spin-like » T.L.S.); then, rather than being interested in the E.S.R. spectrum itself, which reflects the static properties (except at the highest temperatures where the spectrum may be broadened by spin-lattice relaxation), it seems better to concentrate upon the spin-lattice relaxation time and its temperature dependence, which can give informations on the excitations associated with the T.L.S. if the spin-T.L.S. coupling is strong enough. If this coupling is more efficient than the usual spin-phonon coupling, it will moreover be possible to get information at relatively high temperatures, whereas anomalies in the heat capacity and...
thermal conductivity can be detected at low temperatures only. The previous considerations on E.S.R. are equally true for N.M.R. and optical resonant absorption. We now recall the main results gained from these spectroscopic techniques: Rubinstein and Taylor first observed that the nuclear spin-lattice relaxation time $T_{1N}$ was shorter in glassy $\text{As}_2\text{S}_3$ than in the crystalline material [5]. Szeftel and Alloul [6] then observed a similar behaviour in $\text{B}_2\text{O}_3$ and $(\text{Na}_2)_0.9\text{SiO}_2)_0.7$ ($T_{1N}^{+} \propto T^\alpha$ with $\alpha = 1.3 \pm 0.1$ and $1.4 \pm 0.1$ respectively), and at first explained it by a process involving one T.L.S. and one phonon. This was criticized by Reinecke and Ngai [7], who interpreted Szeftel and Alloul's results by a process involving two T.L.S.; in their treatment they assumed that the matrix elements of the electric field gradient (E.F.G.) do not depend upon the T.L.S. energy. More recently, Szeftel and Alloul [8] used new results obtained by Joffrin and Levelut from ultrasonic attenuation [9]; they thus showed that the effective process could not be that suggested by Reinecke and Ngai (two T.L.S. with the same energy must be present near a given nucleus), but consisted of a modulation of the E.F.G. by the nearest T.L.S.

The optical homogeneous linewidth of rare earth ions in some amorphous hosts was similarly found to show an unusual increase with temperature [10, 11]. Lyo and Orbach [12] interpreted the quadratic temperature dependence of the linewidth using a process involving one T.L.S. and one phonon.

Kurtz and Stapleton measured the electron spin-lattice relaxation time of the F centre created by irradiation of the amorphous-like doped $\beta$-alumina up to 30 K (in this crystalline material, dielectric and ultrasonic absorption show the existence of T.L.S. up to 100 K [13]). The usual Raman processes are not observed in this material. Kurtz and Stapleton [14] interpreted their experimental results as a process involving two T.L.S. and one phonon.

In this paper we present experimental results on the electron spin-lattice relaxation of $V^{4+}$ defects present in amorphous $\text{V}_2\text{O}_5$. The situation is rather simple: one deals with a single 3d electron, and the symmetry in $\text{V}_2\text{O}_5$ is low enough to lead to a singlet ground level (no Jahn-Teller effect). The sample, apparatus and experimental results are described in section 2; the dependence of the electron spin-lattice relaxation time $T_1$ versus the temperature $T$ is found to differ greatly from that met in any crystalline material (for clarity, the presentation and discussion of the results for crystalline $\text{V}_2\text{O}_5$ are given elsewhere [15]).

In section 3 we interpret this unusual behaviour by considering that the spins interact with the phonon bath via the T.L.S. Since several symbols have often been used to describe a given physical quantity in the literature using the T.L.S. concept, we thought it useful to describe the T.L.S. model in some detail; whenever possible, we tried to use the symbols which seem to have been most generally accepted; this led us to avoid some of the notations used in [14] for instance. In the case of $V^{4+}$ in $\text{V}_2\text{O}_5$, the mechanism proposed by Stapleton cannot be effective; we discuss the possibility of another mechanism. For crystalline solids it is well known that an exact theoretical determination of $T_1$ is generally a difficult task. For amorphous solids it is really impossible at the present time. We thus adopted the following attitude: we did not try such an exact determination, but used a phenomenological Hamiltonian, and found the temperature dependence of $T_1$; as a second step, we considered a model suggested by the present experimental situation, which is certainly far from the truth, but which should allow at least some crude estimates.

2. Sample, experimental methods and results. — Experiments were carried out on amorphous $\text{V}_2\text{O}_5$, obtained by splat cooling from the melt [16]. When heated above its melting point (650 °C), $\text{V}_2\text{O}_5$ loses oxygen:

$$\text{V}_2\text{O}_5 \rightarrow \text{V}_2\text{O}_{5-x} + \frac{x}{2} \text{O}_2.$$  

This non-stoichiometry remains when cooling the liquid. In the solid, oxygen vacancies are compensated by the existence of vanadium ions in a reduced valence state, mainly $V^{4+}$. This mixed-valence oxide shows semi-conducting properties due to hopping of unpaired electrons between $V^{4+}$ and $V^{5+}$ ions. However, amorphous $\text{V}_2\text{O}_5$ has such a low conductivity for $T < 100$ K ($\rho = 5 \times 10^{11}$ $\Omega$ cm at 100 K) that the unpaired electrons can be considered bound to a given ion in our E.S.R. experiments. In $\text{V}_2\text{O}_5$, a $V^{4+}$ ion is surrounded by six oxygen ions in a bipyramidal configuration (Fig. 1); however, the distance between the $V^{4+}$ ion and oxygen labelled 1 in figure 1 is greater than the other ones; the crystal field from these ions can be considered as having two components, one with octahedral and one with axial symmetry. The $d^1$ configuration is split into a $t_{2g}$ and an $e_g$ level by the octahedral field, and, as the ligands have negative charges, the ground level is the triplet. A distortion of the octahedron along the vertical axis splits the $t_{2g}$

![Image of Vanadium ion and its six nearest neighbour oxygen ions in V2O5. The distances are those of the crystalline oxide. The local order in the amorphous and in the crystalline materials is nearly the same.](image-url)
level into a singlet and a doublet. The E.S.R. spectrum consists of 8 lines corresponding to the hyperfine coupling of the unpaired electron \((S = 1/2)\) of a \(V^{4+}\) ion with a \(^{51}\text{V}\) nucleus \((I = 7/2)\). \(T_1\) was measured by the pulse saturation and recovery method, using an X-band superheterodyne spectrometer previously described [17]. For 1.3 K < \(T\) < 4.2 K the sample was immersed in liquid helium, and the temperature was measured with a GaAs diode placed against the TE\(_{011}\) cylindrical cavity containing the sample. For 3.7 K < \(T\) < 100 K we used an Oxford E.S.R. 9 gas-flow cryostat and carefully checked the temperature. The observed recovery of the absorption signal after a saturating pulse did not depend upon the \(M_i\) value, and was not exponential; it was best fitted by a sum of two exponential terms whose time constants kept a constant ratio of 4 in all the accessible temperature range. One must point out that for \(S = 1/2\) the recovery should be exponential. The observed behaviour remains unclear but cannot be thought of as a consequence of amorphicity since it was observed in crystalline \(V_2O_5\) as well. We called the largest time constant \(T_1\); its temperature variation is shown in figure 2.

One first observes that at the lowest temperatures \(T_1^{-1} \propto T^2\) although in this temperature range one should expect the linear law associated with the usual direct process. This behaviour obviously cannot be attributed to a strong bottleneck since a quadratic dependence is observed up to temperatures as high as 20 K. When \(T > 20\) K, \(T_1^{-1}\) can locally be described by a \(T_1^{-1} \propto T^n\) law, where \(n\) varies from 2 (\(T < 20\) K) to 1 (highest temperatures). The important point is that this is far from the \(H^2 T^n I_a(\theta_a/T)\) or \(T^n I_a(\theta_a/T)\) laws observed for a Kramers system in a crystalline medium; these laws are associated with two-phonon (Raman) processes and both behave as \(T_1^{-1} \propto T^2\) at high temperatures, in contradiction with the tendency to a linear dependence observed in \(V_2O_5\) at the highest temperatures. This indicates that the usual Raman process is negligible even at the highest temperatures of measurements. The analytical expression suggested by our theoretical treatment (see section 3) which gives the best fit with the experimental results is the following:

\[
T_1^{-1} = 39 T^2 \int_0^{56/T} \frac{dx}{\sinh x} (T_1, T, K). \tag{1}
\]

3. Interpretation. — The observed law (1) cannot be associated with any relaxation process known in crystalline materials. On the contrary, a \(T^2\) dependence has already been observed in \(\beta\)-alumina by Kurtz and Stapleton [14] who attributed it to a modulation of the superhyperfine interaction by the T.L.S. In the present case, where no superhyperfine interaction exists, we think that the T.L.S. modulate the crystal field. Before discussing this point we recall the T.L.S. formalism.

A model system frequently considered for a T.L.S. is a particle with mass \(m\) in a one-dimensional asymmetric double-well potential [18]:

\[
V(x) = \begin{cases} 
\frac{1}{2} m d^2(x - d)^2 - \Delta & x < 0 \\
\frac{1}{2} m d^2(x + d)^2 + \Delta & x > 0.
\end{cases}
\]  

(2)

When \(\Delta = 0\) and \(d \to \infty\) this mass may be considered submitted to a single central force, and the corresponding solutions are those of harmonic oscillators; one for the left well (ground state \(\Psi_L\)), and one for the right well (ground state \(\Psi_R\), with the same energy \(\hbar \omega/2\), hereafter taken as the origin of energies). When \(d\) is finite, the particle may tunnel through each well. When \(kT \ll \hbar \omega\) an approximate solution can be found using the variational method inside the subspace spanned by \(\Psi_L\) and \(\Psi_R\); the degeneracy is lifted and the tunnel splitting is \(2 \Delta_0\), where \(\Delta_0 = \hbar \omega \sqrt{\sigma/\pi} e^{-\sigma}\) with \(\sigma = m d^2 / \hbar \omega\). On the contrary, the asymmetry term \(\Delta\) favours localization within one well. When \(\Delta \ll kT\), using the previous assumptions
and supposing a weak overlap between \( \Psi_L \) and \( \Psi_G \), it is found (1) that the static T.L.S. Hamiltonian inside the \( \{ \Psi_L, \Psi_R \} \) basis is

\[
\hat{h} = \begin{pmatrix}
-\Delta & -\Delta_0 \\
-\Delta_0 & +\Delta
\end{pmatrix}.
\]

We call the eigenstates of \( \hat{h} \) \( \Psi_+ \) (energy + \( E \)) and \( \Psi_- \) (energy - \( E \)), with \( E = \sqrt{\Delta^2 + \Delta_0^2} \).

The usual assumption for the density of T.L.S. is that proposed by Phillips [3], with no correlation between \( \Delta \) and \( \Delta_0 \). Instead of \( \Delta \) and \( \Delta_0 \), it is more convenient in our problem to choose \( E \) and \( r = (\Delta_0/E)^2 \) as independent variables. The density is then:

\[
P(E, r) = \frac{P}{2} r^{-1}(1-r)^{-1/2} \quad \text{for} \quad 0 \leq E \leq E_m \\
0 \quad \text{elsewhere}
\]

\( P \) is an experimentally determined quantity of the order of \( 10^{21} \text{ eV}^{-1} \text{ cm}^{-3} \) [3].

As was said earlier, the phonons are strongly coupled to the T.L.S. and modulate their tunnel splitting (for instance by modulating the distance \( 2d \)) and their asymmetry. The corresponding T.L.S.-phonon Hamiltonian \( H_{T,\text{Ph}} \) is represented in the \( \{ \Psi_L, \Psi_R \} \) basis by the matrix:

\[
\begin{pmatrix}
-\frac{\partial \Delta}{\partial e} & -\frac{\partial \Delta_0}{\partial e} \\
-\frac{\partial \Delta_0}{\partial e} & \frac{\partial \Delta}{\partial e}
\end{pmatrix} e
\]

where \( e \) is the strain. (A more accurate description should consider a three-dimensional model, and the tensorial character of the strain.) In the \( \{ \Psi_+, \Psi_- \} \) basis the Hamiltonian \( H = \hat{h} + H_{T,\text{Ph}} \) finally becomes:

\[
H = E_0 G_x + (G'_x \sigma_x + G'_z \sigma_z) e
\]

where \( \sigma_x \) and \( \sigma_z \) are two Pauli matrices acting inside the \( \{ \Psi_+, \Psi_- \} \) space and where (2):

\[
G'_x = \frac{1}{E} \left( -\frac{\partial \Delta}{\partial e} A_0 + \frac{\partial \Delta_0}{\partial e} \Delta \right)
\]

\[
G'_z = \frac{1}{E} \left( \frac{\partial \Delta}{\partial e} A_0 + \frac{\partial \Delta_0}{\partial e} \Delta \right).
\]

We must now express the Hamiltonian \( H_{T,\text{S}} \) describing the spin-T.L.S. coupling. We will set up a phenomenological operator. As the system has an electron spin \( S = 1/2 \) and a nuclear spin \( I = 7/2 \), the most important spin operators having non-zero matrix elements are \( S_A \) and \( H g S \), neglecting the nuclear Zeeman term. If we suppose that \( A \) and \( g \) depend upon the position of the tunnelling entity and if we use a linear approximation then, in the \( \{ \Psi_L, \Psi_R \} \) basis, the interaction \( H_{T,\text{S}} \) has the following expression:

\[
H_{T,\text{S}} = S \Delta \mathbf{A} \mathbf{I} + \beta \mathbf{H} \Delta g S
\]

where \( \Delta \mathbf{A} \) and \( \Delta g \) depend upon the structure of the T.L.S. In the \( \{ \Psi_+, \Psi_- \} \) basis, \( H_{T,\text{S}} \) becomes:

\[
H_{T,\text{S}} = (S \Delta \mathbf{A} \mathbf{I} + \beta \mathbf{H} \Delta g S) \left( \frac{A}{E} \sigma_z - \frac{\Delta_0}{E} \sigma_x \right)
\]

where the first part acts on the spin states, and the second on the T.L.S. states.

The \( \Delta \mathbf{A} \) term is the modulation of the hyperfine interaction by the T.L.S. considered by Stapleton. Such a mechanism may be considered when, for instance, the electron-spin observed by E.S.R. is that of an electron delocalized over several nuclei having a nuclear spin with which it interacts through the Fermi interaction. However in our case, where the electron and the nucleus belong to the same atom, no motion of the nucleus can modulate the hyperfine interaction, and \( \Delta \mathbf{A} \) is strictly zero. We must then consider the effect of the \( \Delta g \) term, describing the modulation of the crystal field. One must first observe that if the spin Hamiltonian is \( \beta \mathbf{H} \mathbf{g} \mathbf{S} \) and if \( \mathbf{g} \) and \( \Delta \mathbf{g} \) have the same principal axes with principal values \( g_x \), \( g_y \), \( g_z \) and \( \Delta g_x \), \( \Delta g_y \), \( \Delta g_z \) respectively, then in the particular case when

\[
\Delta g_x/g_x = \Delta g_y/g_y = \Delta g_z/g_z
\]

the modulation of the crystal field will not induce spin-lattice relaxation. This can be easily seen as follows: the spin Hamiltonian and the spin part of \( H_{T,\text{S}} \) may be written \( \beta \mathbf{g} \mathbf{S} \mathbf{H} \mathbf{S} \) and \( \beta \mathbf{g} \mathbf{S} \Delta \mathbf{g} \mathbf{S} \mathbf{H} \mathbf{S} \) where \( \mathbf{H} \) is an effective field with the same modulus as \( \mathbf{H} \); when (9) is satisfied, \( \mathbf{H}' \equiv \mathbf{H} \) and both Hamiltonians are simultaneously diagonal. In the following we suppose this not to be the case. We use a second-order perturbation, the perturbing Hamiltonian being \( H_p = H_{T,\text{Ph}} + H_{T,\text{S}} \) and consider processes with one phonon and one T.L.S. When an electron undergoes \( 1/2 \rightarrow -1/2 \) transition, energy may be conserved through one of the three following processes: (a) creation of a phonon; (b) creation of a phonon and excitation of a T.L.S.; (c) creation (or destruction) of a phonon and de-excitation (or excitation) of a T.L.S. We consider processes of type (c) only, since (a) and (b) use phonons with energy \( \leq g \beta H \), whose densities of states are very low. We call \( W_{1f} \) and \( W_{1f'} \) the probabilities per unit time for the transitions

\[
| i \rangle = | +, \Psi_+, n \rangle \rightarrow | f \rangle = | -, \Psi_-, n + 1 \rangle
\]
and respectively, where +, - refer to the spin with energy $E_z$, $\Psi_+$, $\Psi_-$ to a given T.L.S. with energy $2E$ and $n$ to a given phonon mode with energy $\hbar \omega$ (Fig. 3):

$$W_{if} = \frac{2\pi}{\hbar} \left| \sum_a \frac{\langle f | H_p | a \rangle \langle a | H_p | i \rangle}{E_i - E_a} \right|^2 \times \delta(E_z + 2E - \hbar \omega) \equiv W_{fi}. \quad (10a)$$

It is easily found that:

$$W_{if} = \frac{8 \pi \beta^2}{\hbar E^2} \left| \langle + | \mathbf{H} \Delta g \mathbf{S} | - \rangle \right|^2 \left| \langle n | e | n + 1 \rangle \right|^2 \left( \frac{\Delta_0 G^r_z}{\hbar \omega} + \frac{\Delta G^r_x}{E_z} \right)^2 \delta = (n + 1) W_1 \delta. \quad (10b)$$

In the same way:

$$W_{rf} = \frac{8 \pi \beta^2}{\hbar E^2} \left| \langle + | \mathbf{H} \Delta g \mathbf{S} | - \rangle \right|^2 \left| \langle n | e | n - 1 \rangle \right|^2 \left( \frac{\Delta_0 G^r_z}{\hbar \omega} - \frac{\Delta G^r_x}{E_z} \right)^2 \delta = (n) W_2 \delta. \quad (11)$$

We call $W_{+-}$ the probability per unit time that a spin initially in the $+$ state make a transition to the state $-$ with the participation of that T.L.S. and of any phonon mode with energy $\hbar \omega$ (the corresponding density being $\rho(\hbar \omega)$) with $\hbar \omega$ and $2E \gg E_z$; we define $W_{-+}$ in the same way:

$$W_{+-} = [W_1 p_+ (n + 1) + W_2 p_- n] \rho(\hbar \omega) \quad (12a)$$

$$W_{-+} = [W_1 p_- n + W_2 p_+ (n + 1)] \rho(\hbar \omega) \quad (12b)$$

where

$$p_- = (1 + e^{-x})^{-1}; \quad p_+ = 1 - p_-; \quad x = \frac{2E}{kT}$$

and

$$n = (e^x - 1)^{-1}.$$ 

In these expressions $E_z$ has been neglected in comparison to $E$, which leads to $W_{+-} \equiv W_{-+}$ but does not affect the determination of $T_1$. We define a spin-lattice relaxation time $T_1$ for that spin and that T.L.S.:

$$T_1^{-1} = W_{+-} + W_{-+} = (W_1 + W_2) \frac{1}{\sinh x} \rho(\hbar \omega). \quad (13)$$

Using a Debye model for the phonons, one gets:

$$T_1^{-1} = \frac{32 \beta^2}{\pi \rho \hbar^2 \nu_{\text{eff}}^3} \left| \langle + | \mathbf{H} \Delta g \mathbf{S} | + \rangle \right|^2 \left( \frac{\Delta_0 G^r_z}{\hbar \omega} \right)^2 \left( \frac{\Delta G^r_x}{E_z} \right)^2 \frac{E}{\sinh 2E/kT} \quad (14)$$

---

**Fig. 3.** — Indirect spin-phonon coupling via the modulation of its $g$ factor by a (phonon-coupled) T.L.S. The spin and T.L.S. both change their state during the transition; in case of $A$ modulation there is moreover a nuclear state change.
We successively discuss the $G'$ and $G_\Sigma$ contributions; in ultrasonic experiments, $G_\Sigma$ is responsible for relaxation attenuation, and $G'$ for resonant attenuation. It is usually thought that $G_\Sigma \approx -\frac{\partial \Delta}{\partial e} \frac{\Delta}{E}$ and $G' \approx \frac{\partial \Delta}{\partial e} \frac{\Delta}{E}$. Using the variables $E$ and $r$, the $G'_z$ contribution turns out to be:

$$
(T^{-1})_{g_z} = \frac{8 \beta^2}{\pi \rho h^2 v_{eff}} \left( -\left| -\frac{\partial \Delta}{\partial e} \frac{\Delta}{E} \right| + \right)^2
$$

$$
\times \frac{\left( \frac{\partial \Delta}{\partial e} \frac{\Delta}{E} \right)^2}{2 E/kT}. \quad (15)
$$

If we take a spin 1/2 with axial symmetry, $H$ symmetry axis, $\Delta g = 2.5 \times 10^{-3}$ (see appendix), $H_0 = 3.000 \, G$, $v_{eff} = 2 \times 10^3 \, m/s$, $\rho = 2 \times 10^3 \, kg/m^3$ and $(\partial \Delta/\partial e) = 1 \, eV [3]$, we obtain:

$$
(T^{-1})_{g_z} = 10^{1.2} H^2 \frac{r(1 - r) E}{\sinh 2E/kT}
$$

$$
(T_1 s, H \, gauss, E \, ergs). \quad (16)
$$

The fastest ratio is obtained when the neighbouring T.L.S. has $r = 1/2$; supposing $r = 1/2$, $T = 10 \, K$, $2 E = kT$, and $H = 3.000 \, G$, we finally get $T^{-1}_{10^6} \approx 600 \, \mu s$. We observe that if $x_M = 2 \, E_m/kT \lesssim 1$ (high temperatures) then $x/\sinh x \approx 1$ and $T_i^{-1}$ does not depend upon $E$ but depends linearly upon $T$. Let us now suppose that each spin has its own relaxation time, imposed by a neighbouring T.L.S.; the recovery signal is then a sum of exponential terms and is proportional to

$$
\int_0^{x_M} dx \int_{r_0}^{r_1} dr \left[ 1 - e^{-T(r,x)P(x,r)} \right] P(x,r)
$$

where

$$
T_i^{-1}(x,r) \propto T_f(r) \frac{x}{\sinh x}.
$$

At high temperatures ($x_M \lesssim 1$) the recovery would strongly depart from an exponential law, because $T_i^{-1}$ still depends upon $r$; the situation would be even worse at low temperatures ($x_M \gg 1$) because of the additional $E$ dependence. Let us for simplicity consider the signal due to all spins characterized by the same $r$ value, which is proportional to

$$
\int_0^{x_M} dx \left[ 1 - e^{-T(x)P(x,r)} \right]
$$

where $T(x) = \frac{1}{x_M} \int_0^{x_M} dx \left[ 1 - e^{-AT(x)/\left(2E/kT\right)} \right]$. We thus define

$$
\bar{T}_1^{-1} = \int_0^{x_M} dx \int_{r_0}^{r_1} dr \frac{T_i^{-1}(x,r)P(x,r)}{\int_0^{x_M} dx \int_{r_0}^{r_1} dr \, P(x,r)}.
$$

Stapleton also used this definition [14]. The $G'_z$ contribution is:

$$
(T_i^{-1})_{g_z} \approx 2 \times 10^{-21} H^2 \frac{\bar{T}_1}{N} \int_0^{x_M} \frac{x dx}{\sinh x}.
$$

where $N$ is the T.L.S. concentration. When $x_M \ll 1$ (low temperatures) $(T_i^{-1})_{g_z} \propto T^2$ while when $x_M \gg 1$ (high temperatures) $(T_i^{-1})_{g_z} \propto T$. Our experimental results can be described by this expression if one chooses $2 E_m/k = 56 \, K$. However this value of $E_m$ seems too small, as it is generally thought to be of the order of 1000 K. We will discuss this point more thoroughly in section 4. Similarly the $G'_z$ contribution to the relaxation time of a spin with a given T.L.S.
is found to be:

\[
(T^{-1})_{g_1} = \left( \frac{2E}{E_x} \right)^2 (T^{-1})_{g_2}. \tag{21}
\]

With the numerical values previously used, one gets

\[
(T^{-1})_{g_1} = 1.3 \times 10^{-22} \frac{r(1-r) E^3}{\sinh 2E/4T} \tag{22}
\]

If \( r = 1/2, E = KT, T = 10 \) K, then \((T^{-1})_{g_1} = 1 \) ms.

The \( G' \) contribution to the average time is

\[
(\bar{T}^{-1})_{g_1} = 10^{-13} T^4 \frac{P}{N} \int_0^{\infty} \frac{x^3}{\sinh x} dx \tag{23}
\]

\[
(\bar{T}^{-1})_{g_2} = 6.3 T^2 \int_0^{\infty} \frac{x}{\sinh x} dx.
\]

Moreover

\[
(\bar{T}^{-1})_{g_1} \approx (\bar{T}^{-1})_{g_2} \approx T. \tag{24}
\]

The ratio of the two integrals is about 5 when \( x_M \ll 1 \) and is 0.3 when \( x_M = 1 \). This indicates that the \( G' \) contribution is predicted to be far more important than that from the \( G' \) term. Actually, this was not observed in \( V_2O_5 \) since we did not observe a \( T^4 \) dependence at low temperatures. We recall that our result was obtained by assuming that in \( G' \),

\[
\frac{\partial A}{\partial e} \ll \frac{\partial A}{\partial e} \tag{25}
\]

A possible explanation of this discrepancy could be the fact that, for still unknown reasons, the quantities \( \Delta^2 \left( \frac{\partial A_0}{\partial e} - \frac{\partial A}{\partial e} \right)^2 \) has a very small value. Before concluding, some comments on the modulation of the superhyperfine interaction considered by Stapleton are needed. Let us consider the simple case \( S = 1/2, I = 1/2 \), axial symmetry for \( A \), and \( A/\beta BH \ll 1 \). When \( \Delta A_0 \) is not zero, relaxation takes place simultaneously with the flip of both the electron and the nuclear spins (Fig. 4). We choose the same quantization axis for \( S \) and \( I \). When the \( S_A \) and \( I \) states are not true eigenstates of the superhyperfine interaction, \( S \) and \( I \) must be allowed to change when the \( A \) field is modulated. This hyperfine modulation induces transitions between levels 1 and 3 only, with a probability

\[
W = \frac{2 \Delta A_1^2}{\pi \rho h^* \nu_{eff}} \left[ \frac{(\Delta \rho G' z)^2}{h\omega} + G'(x)^2 \right] \frac{E}{\sinh 2E/4kT}. \tag{25}
\]

If we saturate the \( 1 \leftrightarrow 3 \) E.S.R. transition by a rf pulse and if we neglect the 1-2 and 3-4 nuclear relaxation transitions, there is no way for the recovery of the E.S.R. signal. If one then takes the nuclear probabilities \( w = kW \) into account (where \( W \) is the electron probability, and \( k \ll 1 \)) we find that the population difference \((p_1 - p_4) \) recovers as:

\[
(p_1 - p_4) \approx (p_1 - p_4) \left[ 1 - \frac{1}{2} (e^{-wT} + e^{-2wT}) \right], \tag{26}
\]

which means that the amplitude of the \( e^{-2wT} \) term is zero to first order. In fact the \( |M_1, M_2| \) states are not true eigenstates of the superhyperfine interaction, \( A \) and \( |M_1, M_2| \) states is about 2 \( \times 10^{-7} \). We think therefore that the occurrence of an efficient hyperfine modulation is rather uncommon, because it has to fulfill the condition \( \Delta A/|A \beta BH| \gg 1 \).

4. Conclusion. — The quadratic dependence of the spin-lattice rate of \( V^{4+} \) in amorphous \( V_2O_5 \) observed up to 20 K, and the existence of a 56 K characteristic energy, have been interpreted as resulting from the interaction of the crystal field by the T.L.S., leading to a one phonon and one T.L.S. process. Two main questions arose: what is the meaning of this characteristic energy and why was the \( T^4 \) term predicted by the model unobserved? It is useful to discuss some of the assumptions made. For instance it is thought, after Phillips [3], that \( f(A) \) in \( P(A, A_0) = f(A) g(A_0/A) \) is Gaussian, with a \( 10^{-2} \) eV width. We approximated it by a rectangular function, with half-width \( \Delta_0 \) and calculated \( \bar{T} \), taking the usual integration domain defined in (4); this procedure is in fact valid when \( kT \ll \Delta_0 \) only. A more accurate determination (Appendix II) leads to the following results:

- at low temperature \( (kT \ll \Delta_0) \) our previous results are not modified;
- at high temperature \( (kT \gg \Delta_0) \) expression (20) is still valid, providing that one replaces \( E_0 \) by \( \Delta_0 \).
in the integral. This shows that spin-lattice relaxation measurements can give information on the upper limit of the asymmetry. It is not possible at the present time to give an unquestionable explanation of the absence of the \( T^4 \) term. We have suggested that it may result from a weak average value of \( E^2 A^2 G^2 \). In order to get a better understanding of this point, it would be useful to have more information on \( G_x \), and to perform spin-lattice measurements on \( V_2O_5 \) at other frequencies, and on other amorphous materials.

It must finally be pointed out that the diffusion assumption was used in the theoretical derivation leading to expression (19). This was justified for our rather concentrated material. It is however not obvious that this law would still be observed at the concentrations usually met in electron spin-lattice relaxation experiments, for instance \( 10^{-4} \). It is unfortunately not possible to get lower \( V^{4+} \) concentrations in the amorphous \( V_2O_5 \) obtained by splat-cooling.

**Appendix I.** — In \( V_2O_5 \), the electric field created upon the \( V^{4+} \) ion (3d\(^1\)) by its six oxygen ligands has \( C_{4v} \) symmetry. The electric potential can be developed in spherical harmonics: keeping only the part \( \mathcal{U} \) which has non-zero matrix elements inside the 3d\(^1\) configuration, one gets:

\[
\mathcal{U} = V_0 + \frac{\alpha r^4}{4} \left[ Y_2^0 + \frac{5}{14} (Y_4^0 + Y_4^{-4}) \right] + \frac{\beta r^2}{4} Y_2^2 + \frac{\gamma r^4}{4} Y_4^0 + \frac{\delta r^4}{4} (Y_4^0 + Y_4^{-4}).
\]  

(1.1)

In the \( \{ |2>, | -2>, |0>, |1>, |1>, | -1> \} \) basis, the crystal field Hamiltonian is found to be:

\[
\begin{align*}
Dq - 2A + B & \quad 5Dq + 5C \\
5Dq + 5C & \quad Dq - 2A + B \\
6Dq + 2A + 6B & \quad -4Dq + A - 4B \\
-4Dq + A - 4B & \quad -4Dq + A - 4B
\end{align*}
\]

where

\[
Dq = \frac{\Delta}{10} = \frac{\delta r^4}{14\sqrt{\pi}}, \quad A = \frac{\sqrt{5} \beta r^2}{14\sqrt{\pi}} \\
B = \frac{\gamma r^4}{14\sqrt{\pi}}, \quad C = \frac{\delta r^4}{70\sqrt{\pi}}.
\]

In \( O_2 \) symmetry \((A = B = C = 0)\) the 3d\(^1\) configuration splits into a ground triplet \((t_2^g\) energy \(-4Dq)\) and a doublet \((e_g\) energy \(6Dq))\). In \( C_{4v} \) symmetry the triplet is split into a singlet \((\sqrt{2})\) state with energy \(-4Dq - 2A + B - 5C\) and a doublet \((| + 1> \) and \(| - 1> \) states with energy \(-4Dq + A - 4B)\) separated from the singlet by an energy \(\delta = 3A - 5B + 5C\), and the doublet is split into two singlets \((\sqrt{2})\) state with energy \((6Dq - 2A + B + 5C)\), and \(|0>\) with energy \((6Dq + 2A + 6B)\). Whether the ground level is a singlet or a doublet depends upon the relative sizes of \(A, B\), and \(C\). We suppose here that the ground level is a singlet. From second-order theory, the \( g \) tensor is expressed as \( g = g_e I - 2i\lambda A \), where \(g_e = 2.0023\), \(\lambda\) is the spin-orbit coupling constant, and the \(A_{ij}\) component of the \( A \) tensor is

\[
A_{ij} = \sum_x \frac{\langle g | L_i | \alpha \rangle \langle \alpha | L_j | g \rangle}{E_x - E_g}
\]  

(1.2)

\(|g>\) being the ground singlet. In the present case, \(g_{||}\) has axial symmetry, and

\[
g_{||} = g_e - \frac{8\lambda}{\Delta}, \quad g_{\perp} = g_e - \frac{2\lambda}{\delta}.
\]  

(1.3)

If one takes \(\Delta = 20000\) cm\(^{-1}\), \(\delta/\Delta = 1\), and \(\lambda = 250\) cm\(^{-1}\), then \(g_e - g_{||} = 0.1\) and \(g_e - g_{\perp} = 0.025\). This is not too far from the experimental values for \(V^{4+}\) in amorphous \( V_2O_5 \) \((g_{||} = 1.936, g_{\perp} = 1.987 [19])\). We then consider that the \( g \) tensor is modulated by the tunnelling of a neighbouring T.L.S. The simplest \( g \) modulation one can imagine corresponds to the following variation of the potential parameters:

\[
\begin{align*}
\frac{\delta A}{A} & = \epsilon \\
\frac{\delta A}{A} & = \frac{\delta B}{B} = \frac{\delta C}{C} = \eta
\end{align*}
\]

then

\[
\frac{\Delta g_{||}}{g_e - g_{||}} = \epsilon, \quad \frac{\Delta g_{\perp}}{g_e - g_{\perp}} = \eta.
\]  

(1.4)

If \(\epsilon = \eta = 0.1\), \(\Delta g_{||} = 10^{-2}\) and \(\Delta g_{\perp} = 2.5 \times 10^{-3}\). These results are still valid for a 3d\(^1\) ion in \( D_{4h} \) symmetry.

**Appendix II.** — In the T.L.S. model, \( P(A, A_0) \) is defined in a rectangular domain (Fig. 5a). In general the theoretical determination of physical quantities
The allowed values for the tunnel splitting $\Delta_0$ and the asymmetry $A$ define a rectangular domain of definition in $(\Delta_0, A)$ coordinates, represented in figure 5a. When one changes to $(r, E)$ coordinates, with $r = (\Delta_0/E)^2$ and $E = \sqrt{\Delta_0^2 + A^2}$, the corresponding domain of integration changes to that of figure 5b.

Fig. 5. — The allowed values for the tunnel splitting $\Delta_0$ and the asymmetry $A$ define a rectangular domain of definition in $(\Delta_0, A)$ coordinates, represented in figure 5a. When one changes to $(r, E)$ coordinates, with $r = (\Delta_0/E)^2$ and $E = \sqrt{\Delta_0^2 + A^2}$, the corresponding domain of integration changes to that of figure 5b.

has been made under the assumption of a low temperature $(kT \ll \Delta_M$ and $\Delta_{OM})$. At higher temperatures, one must take care of two important points:

1) one supposes that $\Delta_M \ll \Delta_{OM}$. As a consequence one may note that for instance the usual expression for the density of states $n(E) = A \log \frac{2E}{\Delta_{OM}}$ [3] is no longer valid when $\Delta_M < E \leq \Delta_{OM}$;

2) the domain where $P(E, r)$ is defined is not rectangular, as written in (4), but has a more complicated shape (Fig. 5b). This has some consequences on the $\overline{T}_1^{-1}$ determination: we consider here the $G_2$ term only. We found that $\overline{T}_1^{-1} = A \frac{(1 - r) E}{\sinh 2E/kT}$ and we get:

$$\overline{T}_1^{-1} = A \frac{\overline{P}}{2 \cdot N} \left[ \int_0^{\Delta_{OM}} \frac{E \, dE}{\sinh 2E/kT} \int_{r_0}^1 \sqrt{1 - r} \, dr + \int_{\Delta_M}^{\Delta_{OM}} \frac{E \, dE}{\sinh 2E/kT} \int_{1-(\Delta_M/E)^2}^1 \sqrt{1 - r} \, dr \right] = (1 + \alpha) \frac{\overline{P} \, kT}{3 \cdot N} \left( \frac{1}{2} \right) \int_0^{\Delta_M/kT} \frac{x \, dx}{\sinh x}. \tag{II.1}$$

where

$$\alpha = \left( \frac{2 \cdot \Delta_M}{kT} \right) \left( \frac{\Delta_M/kT}{\sinh \Delta_M/kT} \right).$$

If $T \to 0$, $\alpha \to 0$; if $T \to +\infty$, $\alpha \to 1/2$; when $2 \Delta_M/kT = 1$, $\alpha \approx 1$. This means that expression (20) is still valid providing that $E_m$ be replaced by $\Delta_M$ in the integral.

References