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TEMPERATURE DEPENDENCE OF THE SPIN-LATTICE RELAXATION TIME OF V^{4+} *IN* TiO_2

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The temperature dependence of the spin-lattice relaxation time τ_1 of V^{4+} in TiO_2 has been measured in the range 4.2 to 110°K. Above 50°K relaxation proceeds via the excited state, 650 cm^{-1} above the ground state.

A recent EPR (electron paramagnetic resonance) investigation of rutile (TiO_2) containing vanadium showed that the vanadium enters the crystalline lattice of rutile as a V^{4+} ion, which is isoelectronic with Ti^{3+}.[1,2]

The Ti^{3+} ion has highly different EPR spectra in different salts. In alums and corundum the resonance lines of this ion can be observed only at liquid helium temperature and have a highly anisotropic g-factor that is quite different from the pure spin value g = 2.[3,4] In other salts (e.g., Ti $[(CH_3CO)_2CH_3]$) the g-factor anisotropy is weaker, its value is closer to 2, and resonance can be observed at liquid nitrogen temperature and even at room temperature.[5]

This difference in behavior is due to the energy level structure of Ti^{3+} in fields of different crystalline lattices. A field of cubic symmetry splits the five-fold degenerate lowest orbital level of ^2D into a lower triplet and an upper doublet. A crystalline field of lower symmetry splits the lower triplet into a singlet and a doublet. If the orbital doublet is lower in the crystalline field, we find a strongly anisotropic g-factor and short relaxation times; if the singlet is lower, the g factor is close to 2, and the spectrum can be observed at high temperatures.

The latter case occurs for V^{4+} in TiO_2 (Fig. 1). The spectrum is observable both at helium and nitrogen temperatures, and the g-factors are close to g = 2 with little anisotropy ($g_z = 1.955$; $g_x = 1.913$; $g_y = 1.912$).[1]

This paper gives the results of an investigation of the spin-relaxation process of V^{4+} at different temperatures. The data confirm the ideas presented above about the disposition of the energy levels.

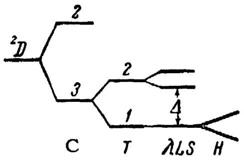

FIG. 1. Splitting of the bottom ^2D term of V^{4+} in crystalline fields of different symmetry: C – cubic symmetry, T – tetragonal symmetry, λLS – effect of spin-orbit coupling, H – external magnetic field.

EXPERIMENTAL METHOD

The spin-lattice relaxation times in the temperature interval 4.2 to 50°K were measured by the pulse method at 9.4 Gc/sec. A superheterodyne spectrometer was employed with a reflection-type cavity, a circulator, and a third, saturating klystron. Powerful saturating pulses were supplied from the klystron at different frequencies, from 1 to 300 cps, depending on the magnitude of the spin-relaxation time. The lengths of the pulses varied from 10 μsec to 1 msec. The exponential restoration of the EPR line intensity after the action of the saturating pulse was recorded on a pulsed oscillograph. The duration of the tail of the pulse, which determines the time resolution of the arrangement, was 0.5 μsec.

The sample was placed in a temperature-regulated cavity, described previously.[6] The temperature in the interval 4.2 to 50°K was measured with a carbon thermometer, and at higher temperatures with a resistance thermometer of copper wire. Calibration of these thermometers was effected with a gas thermometer.

For T > 50°K, measurements by the pulse method were impossible, since the time τ_1 becomes comparable to the resolution time of the apparatus. In the interval 70 to 110°K, accurate measurements were made of the broadening caused by spin-lattice relaxation. In order to calculate the spin-lattice relaxation time from these measurements, it is necessary to take into account the initial line width ΔH_0, independent of temperature, caused by the dipole-dipole interaction, irregularities in the crystalline field, etc. The value of ΔH_0 was measured at 50°K, since there was no further narrowing below this temperature (Fig. 2).

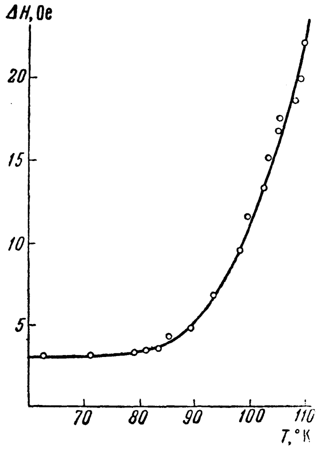

FIG. 2. Temperature dependence of line width of V^{4+}.

The calculation of the initial width can be carried out in various ways, depending on the character of the initial broadening of the line. For a homogeneously-broadened line the half-width

$$\Delta H = \Delta H_0 + \Delta H_{\mathrm{sl}}\ , \tag{1}$$

where ΔH_{sl} is the width caused by the spin-lattice relaxation. When ΔH_0 is caused by inhomogeneous broadening, the half-width

$$\Delta H \approx \sqrt{(\Delta H_0)^2 + (\Delta H_{\mathrm{sl}})^2}. \tag{2}$$

Obviously, at high temperature, where $\Delta H_{sl} \gg H_0$, both formulas give like results.

In our case the concentration of paramagnetic ions was very low (0.01%), and, in addition, the ions were distributed over the various sub-levels of a hyperfine structure; hence the resonant dipole-dipole interaction could not explain the observed initial line width. It is more probable, therefore, that the initial line width is inhomogeneous in nature. To verify this presumption and its consequence, Eq. (2), measurements of τ_1 by the saturation method were carried out in the temperature interval 50—70°K, thus "joining up" the results obtained for τ_1 by the various methods. The absolute values of the relaxation time found by the continuous saturation method for single crystals of rutile are frequently in error, because of the uncertainty in evaluating the intensity of the high-frequency magnetic field in the sample, which has a remarkably high dielectric constant. However, relative measurements of τ_1 in a narrow temperature interval are sufficiently accurate.

Checking by the continuous saturation method showed that the data of the different methods were in good agreement, i.e., the calculation of the initial line width was correct.

TEMPERATURE DEPENDENCE OF τ_1

All the measurements were made on rutile crystals oriented so that the tetragonal C axis was parallel to the external magnetic field. Measurements on different hyperfine components gave practically the same results. The temperature dependence of τ_1 is shown in Fig. 3a.

In the range 4.2—10°K, τ_1 is inversely proportional to T within the limits of experimental error; this is characteristic of a spin-lattice relaxation process of the first order.

For temperatures from 10 to 50°K, τ_1 depends on temperature more strongly, the dependence having the form $\tau_1 \sim T^{-n}$, where n = 5.5. Above 50°K there is a departure from this dependence. Above 70°K τ_1 is described well by the formula

$$\tau_1 = 6 \cdot 10^{-12} \exp{(\Delta/kT)}\ \mathrm{sec} \tag{3}$$

where $\Delta = 650\ \mathrm{cm}^{-1}$. The dependence of τ_1 on the reciprocal of the temperature above 70°K is given in Fig. 3b, where the expression (3) is shown by a straight line. The accuracy of the line broadening measurements[1)] did not permit the determination of the magnitude of Δ to better than 100 cm^{-1}.

At temperatures above 10°K spin-lattice relaxation occurs via second-order processes. The expected theoretical dependence for V^{4+} is $\tau_1 \sim T^{-7}$. The existence of an exponential dependence above 70°K is attributed to a resonance mechanism for spin-lattice relaxation via an excited state, such as has been observed in magnesium cerium nitrate.[7] A similar relaxation mechanism has been reported many times for both iron-group and rare-earth salts.

The parameter Δ determined from $\tau_1(T)$ is interpreted as the distance to the excited state of V^{4+}.

We note one peculiarity in our case. The two-quantum spin-lattice relaxation mechanism usually occurs when $\Delta < k\Theta$, where Θ is the Debye temperature of the lattice. Only in this case is there a sufficient number of phonons with energies $\hbar\omega = \Delta$ to bring about transitions between the ground

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[1)] A measurement of the dependence $\tau_1(T)$ at a frequency of 14 Gc/sec and higher spectrometer sensitivity gave the value $\Delta = 620 \pm 50\ \mathrm{cm}^{-1}$.

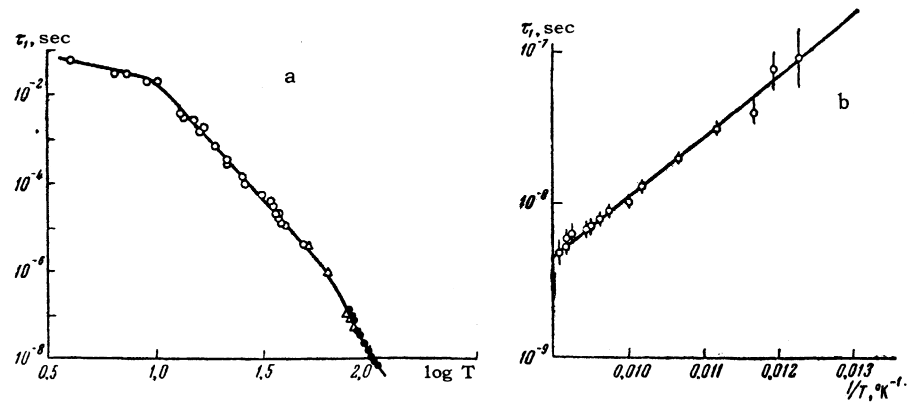
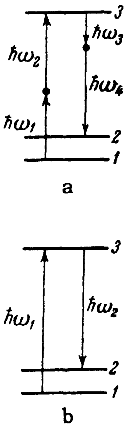


FIG. 3. Temperature dependence of the spin-lattice relaxation time τ_1 of V^{4+}: a – combined graph: ○ – by the pulse method; △ – by the saturation method; ● – by the line-broadening method; b – temperature region 80–110° K, by the line-broadening method.

and excited states. In the previous cases resonant relaxation processes were observed for levels 20–200 cm^{-1} from the ground level.

In our case $\Delta = 650\ cm^{-1}$ (this corresponds to a temperature $\Delta/k = 930°K$), and the condition $\Delta < k\Theta$ is not fulfilled.²⁾ Thus, in the Debye approximation there should not be any acoustic phonons with energies of 650 cm^{-1} in the rutile lattice.

However, the spectrum of phonons of the optical branch has a broad maximum centered near 21 μ, as data on the surface reflection coefficient of rutile in the infrared region show.[9] Thus, spin-lattice relaxation of V^{4+} in TiO_2 at temperatures greater than 70°K can proceed with the participation of optical phonons. There is also the relaxation mechanism of higher order considered earlier by Bashkirov,[10] which also leads to an exponential temperature dependence. In this case four phonons at once participate in the relaxation process (Fig. 4a). Calculations show that for $\Delta \gg kT$ the probabilities of spin-lattice relaxation $w_{13}, w_{23} \sim \exp(-\Delta/kT)$,[10] just as in the case of ordinary two-quantum relaxation (Fig. 4b). Thus, a four-quantum process brought about by acoustic phonons can also explain the exponential temperature dependence of the relaxation time. It is, however, a higher-order process. The question of which of these mechanisms is responsible for the relaxation in this case requires some concrete calculations.



a

b

FIG. 4. Mechanisms of spin-lattice relaxation via excited states: a – four-quantum process; b – two-quantum process.

The value of Δ determined from measurements of τ_1 can be used to interpret the values of the g factors. However, as has already been noted,[11] the observed g factors are successfully explained merely by assuming a very small value for the spin-orbit coupling parameter λ. Thus, if the difference between g_x and g_y is neglected, i.e., if tetragonal symmetry is assumed, and one uses the approximate formulas of Bleaney for Ti^{3+}, then values of g close to those observed ($g_{\parallel} = 1.96$, $g_{\perp} = 1.91$) are obtained for $\lambda \sim 30\ cm^{-1}$.

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[2)] The Debye temperature of the TiO_2 lattice is 670° K (according to heat capacity measurements in the temperature range 68–290° K).[8]