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# TEMPERATURE DEPENDENCE OF THE SPIN-LATTICE INTERACTION FOR $Gd^{3+}$ IN $ThO_2$ AND $CeO_2$

S. B. Oseroff and R. Calvo*

Centro Atómico Bariloche, Comisión Nacional de Energía Atómica
Instituto de Física Balseiro, Universidad Nacional de Cuyo
S.C. de Bariloche, Argentina

The second and fourth order spin-lattice coefficients of $Gd^{3+}$ in cubic positions of $ThO_2$ and $CeO_2$ crystals have been measured as a function of temperature between 4 and 360°K in electron paramagnetic resonance experiments in uniaxially stressed crystals. Important differences in magnitude are obtained for each of the second order coefficients in both lattices and these coefficients show a large variation with temperature. A detailed theoretical calculation of these coefficients has not been carried out; however it is possible to qualitatively interpret the observed temperature variation in terms of explicit contributions coming from the modulation of the orbit-lattice interactions by the lattice vibrations. The temperature variation curves are explained using an Einstein model for the vibrations of the oxygen ligands of the paramagnetic ions. The fourth order coefficients are similar for both crystals and are temperature independent in the studied range. The coefficient related to the effect of a hydrostatic strain on the energy levels of the ion is used to explain the observed temperature variation of the cubic field parameter in terms on implicit contributions coming from the thermal expansion of the crystal.

* Member of the Carrera del Investigador Científico, Consejo Nacional de Investigaciones Científicas y Técnicas, República Argentina.

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## I - Introduction

The interpretation of the crystal field splittings of ions with a half filled shell of electrons, $Cr^{+}$ , $Mn^{2+}$ and $Fe^{3+}$ of the 3d group and $Eu^{2+}$ , $Gd^{3+}$ and $Tb^{4+}$ of the rare earth group, has showed serious difficulties. The crystalline electric field acting alone can not remove the degeneracy of the ground level of these S-state ions and it is necessary to consider high order processes involving spin dependent interactions together with the crystalline field. A great deal of experimental information obtained by electron paramagnetic resonance techniques (EPR) exist for these ions and many theoretical papers dealing with this problem are found in the literature. The reader is referred to Refs. 1 and 2 where an important part of the theoretical work done on this problem until 1966 is quoted. Important progress have been made on the understanding of the S-state iron group ions and, even if a well fit between theory and experiments do not exist yet, an order of magnitude agreement have been found with the experimental parameters.[2]

However, less progress have been made in the explanation of the splittings of the ground state of the rare earth S-state ions, even if experimental data exist in several cubic crystals[3] and in many lattices of lower symmetry.

An attempt to estimate the ionic contributions to the ground state splitting of trivalent gadolynium in lanthanum ethyl sulphate have been done by Wybourne.[1] He consider the contributions coming from several mechanisms involving the crystal field with other interactions in different orders of perturbation and also relativistic effects, configuration mixing and non

linear electrostatically correlated crystal field interactions. The result of the calculation do not agree with the experimental values and Wybourne suggest that the correct explanation should involve the detail of the interaction of the gadolynium ion with the ligands.

It appears to us that additional experimental data, obtained by more sophisticated EPR techniques, where the variation of the splitting of the ion could be measured as a function of some other parameters, should be of help for a better understanding of the mechanisms contributing to the splitting. The measurement of the splitting or shifts of the energy levels of the ions when the crystal is deformed by an external applied stress has proved to be a powerful method for this purpose.[4] In cubic crystals additional components of the crystalline field with cubic, tetragonal and trigonal symmetry with variable magnitude are introduced by the strain and the induced splittings or shifts of the energy levels of the ion can be deduced from the shifts in magnetic field of the EPR lines. The uniaxial stress method allows to evaluate the spin-lattice coefficients which, in a spin Hamiltonian formalism give the strength of the coupling of the ion with the deformation of the lattice. The knowledge of these coefficients is an important piece of information which can be used as a further check of the models.

Uniaxial stress experiments in S-state ions in cubic crystals have been performed by Feher[4] for the iron group and by Calvo et al.[5] for the rare earths. The spin lattice coefficients of the iron group ions $Mn^{2+}$ and $Fe^{3+}$ in MgO have been calculated by Sharma et al.[2] who obtained a reasonable agreement with the experimental values[4]; they found that the main contribution comes from a process originally proposed by Blume and

Orbach[6] which involves the admixtures to the ground state of excited terms which are mixed by the cubic field, by the spin orbit interaction. Because of this admixture it is possible to destroy the degeneracy of the ground level with the electric field induced by the deformation. In a previous work[7] we calculated the contribution of the Blume and Orbach mechanism to the spin-lattice coefficients of $Gd^{3+}$ in $CaF_2$. Some agreement was found only for the second order trigonal coefficient; the calculated value is three times smaller than the experimental, a difference which could be understood by considering the errors which can be introduced by the point charge model used to evaluate the orbit-lattice interaction.

In this paper we report data taken with the uniaxial stress method which can be of help for the understanding of the zero field splitting of the rare earth S-state ions. The spin-lattice coefficients of $Gd^{3+}$ in cubic positions of $ThO_2$ and $CeO_2$ crystals have been measured between helium and room temperature[8]. The two second order spin-lattice coefficients, related to tetragonal and trigonal deformations and the three fourth order coefficients, related to hydrostatic, tetragonal and trigonal deformations have been measured within this range. The three fourth order coefficients remain unchanged in this temperature range within the experimental errors, and are practically equal for both crystals. In contrast the two second order spin-lattice coefficients show very large changes with temperature and, in the case of $Gd^{3+}$ in $CeO_2$, the trigonal coefficient changes the sign as the temperature is varied. Also, even if the amount of the change with temperature is the same for each parameter in both crystals, the absolute values at the same temperature are quite different for the tetragonal and trigonal coefficients.

The changes with temperature of the second order spin-lattice coefficients are explained cualitatively as produced by a phonon induced mechanism (explicit effect).[9] Implicit effects[9] due to the changes of the elastic constants with temperature or to the lattice expansion seem to be unimportant in these cases. Then, our results indicate that any study of the spin-lattice coefficients of rare earth S-state ions should consider the coupling of the ion with the lattice vibrations.

Using our value for the fourth order spin-lattice coefficient related to hydrostatic deformations for $Gd^{3+}$ in $ThO_2$ we show that the temperature variation of the cubic field parameter is due to implicit effects as a consequence of the thermal expansion of the crystal.

## II - Apparatus and Experimental Procedure

The data was taken with a conventional homodyne spectrometer working at 32 GHz. The stress system, which have been described previously,[10] consist mainly of a TE 011 cilindrical microwave cavity where the sample is in the center on a quartz pedestal; a pushrod coming from the head of the cryostat allows to stress the sample against the pedestal by putting weights on the top. The system was designed and built in order to minimize any change of the orientation of the sample when the stress is applied, which is the main cause of error in these measurements[5].

The samples were grown by C. B. Finch of Oak Ridge National Laboratory and have about 0.1% of gadolynium ions which are mostly at cubic positions replacing the $Th^{4+}$ and $Ce^{4+}$ ions in the crystals. They were polished to a prismatic shape of about (1x1x1,5) $mm^3$, where the orientation of the prism, a $[110]$ direction, is accurately defined by the intersection of two (11) natural cleavage faces of the sample. The stress was applied along this $[110]$ direction within an estimated error smaller than 1°. The data was taken for the magnetic field perpendicular to the stress, in the (110) plane. The values of the spin lattice coefficients were obtained from the measurement of the shifts of the seven fine structure lines of the $Gd^{3+}$ cubic spectra as a function of the applied stress for the magnetic field $H_o$ in the three principal direction $[001]$, $[1\bar{1}0]$ and $[111]$. These directions were accurately defined by looking in the screen of an oscilloscope the maximun or minimun of the splittings of the spectra when $H_o$ is rotated in the (110) plane. The shifts for a fourth direction of $H_o$ were measured in some cases as a verification of the results. No set of values was considered until the agreement between the observed shifts and those calculated with

the obtained spin lattice coefficients was within the experimental errors for the seven fine structure lines for the three orientations of $H_o$. The shifts in magnetic field were measured with the sweeping device of the Hall probe-controlled magnet, whose linearity and calibration was checked with a proton resonance magnetometer. The temperature at the non fixed points was measured with a copper resistance with a error smaller than 3° K.

Stresses up to $600 \frac{Kgr}{cm^2}$ were applied to the samples and it was verified in each case the linearity between the shifts in magnetic field and the applied stress.

III - Experimental Results

The EPR spectra of $Gd^{3+}$ in cubic positions of $ThO_2$ and $CeO_2$ crystals have been described with great detail by Abraham et al.[3,11]: intense signals with very narrow linewidths are observed and then they are excelent systems to perform precise measurements.

The uniaxial stress data was explained with the spin-lattice Hamiltonian proposed in Ref. 5; in a slightly different notation:

$$H_{s-\ell} = \sum_{\substack{n,\xi \\ i,\alpha}} G_i^{(n,\xi)} \; O_{i,\alpha}^{(n,\xi)} \; \varepsilon_{i,\alpha} \qquad (1)$$

where the $\varepsilon_{i,\alpha}$ are linear combinations of the strain tensor transforming like the $\alpha$ component of the i-irreducible representation of the cubic group. The $O_{i,\alpha}^{(n,\xi)}$ are linear combinations of the Stevens' equivalent spin operators[12] transforming accordingly; $\xi$ stays for the case where there are more than one n-order operator transforming like $\Gamma_{i,\alpha}$. The $G_i^{(n,\xi)}$ are the n-order spin lattice coefficients. Because of the properties of the strain tensor, a homogeneous strain on the crystal can produce only hydrostatic $(\Gamma_{1g})$, tetragonal $(\Gamma_{3g})$ and trigonal $(\Gamma_{5g})$ deformations of the crystal around a paramagnetic ion in a cubic position. For $Gd^{3+}$ is $S = 7/2$ and n can be 2, 4 and 6; two second order, three fourth order and four sixth order spin-lattice coefficients contribute to $H_{s-\ell}$ in Eq. (1). However as it was reported previously[5] only second and fourth order terms in $H_{s-\ell}$ give measurable contributions to the shifts.

The explicit form of $H_{s-\ell}$ up to fourth order terms when the stress is applied along the $[110]$ direction is:

$$H_{s-\ell} = G_{1g}^{(4)} \left(O_4^o + 5\, O_4^4\right) \varepsilon_{1g} + \left[ G_{3g}^{(2)} O_2^o + G_{3g}^{(4)} \left(O_4^o - 7\, O_4^4\right) \right] \varepsilon_{3g,\theta}$$

$$+ \left[ G_{5g}^{(2)} O_2^2 (s) + G_{5g}^{(4)} O_4^2 (s) \right] \varepsilon_{5g,\zeta} \qquad (2)$$

where the $O_n^m$ and its matrix elements are given by Hutchings[13] and $\varepsilon_{1g} = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$, $\varepsilon_{3g,\theta} = \frac{1}{4}\left(2\,\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}\right)$ and $\varepsilon_{5g\,\zeta} = \varepsilon_{xy}$ .

In the experiments we measure the external stress $P$ rather than the local deformation. It is more realistic then, to use spin-lattice coefficients related to stress rather to strain[4] ; if $s_{11}$, $s_{12}$ and $s_{44}$ are the three elastic constants at the position of the impurity, the spin-lattice coefficients related to stress are defined by[5] :

$$\begin{aligned} C_{1g}^{(n)} &= G_{1g}^{(n)} \left(s_{11} + 2\, s_{12}\right) \\ C_{3g}^{(n)} &= G_{3g}^{(n)} \left(s_{11} - s_{12}\right) \\ C_{5g}^{(n)} &= G_{5g}^{(n)}\, s_{44} \end{aligned} \qquad (3)$$

In this notation the spin lattice Hamiltonian of Eq. (2) can be written as:

$$H_{s-\ell} = C_{1g}^{(4)} P \left(O_4^o + 5\, O_4^4\right) - \frac{1}{4} C_{3g}^{(2)} P\, O_2^o - \frac{1}{4} C_{3g}^{(4)} P \left(O_4^o - 7\, O_4^4\right)$$
$$+ \frac{1}{2} C_{5g}^{(2)} P\, O_2^2 (s) + \frac{1}{2} C_{5g}^{(4)} P\, O_4^2 (s) \qquad (4)$$

and the shifts for $H_o$ parallel to the three directions $[001]$ , $[1\bar{1}0]$ and $[1\bar{1}1]$ are obtained from the formulas in Ref. (5) and (14).

In Figs. 1 and 2 we show the experimental shifts for $Gd^{3+}$ in $ThO_2$ at 295°K and $P = -1$ dyne/cm$^2$ ($P$ is negative because the crystal is compressed in the experiments) for $H_o$ parallel to $[001]$ and $[1\bar{1}1]$

respectively together with the calculated contributions coming from each term of the spin-lattice Hamiltonian. Similar agreement was found for $H_o // [\bar{1}10]$. The same measurements were performed for $Gd^{3+}$ in $ThO_2$ and $CeO_2$ at different temperatures between 4 and 360°K. The values obtained for the spin-lattice coefficients in both crystals at room temperatures are given in Table I; the second order coefficients $C_{3g}^{(2)}$, and $C_{5g}^{(2)}$ in both crystals are given in Figs. 3 and 4 as a function of temperature. The fourth order coefficients are constant, within the experimental errors, between 4 and 360°K and are given in Table I. The errors in the measurement of the shifts of the lines were obtained from the dispersion of the data; from these values, the system of equations which give the shifts of the lines for different orientations of $H_o$ as a function of $P$ and the spin lattice coefficients, we obtained the errors given in Table I and Figs. 3 and 4; any systematic error (orientation of $P$ and $H_o$, changes of position of the sample when stressed, errors due to friction of the pushrod which transmit the force $P$ to the sample, etc.) are well inside of those given there.

No changes of the gyromagnetic factor $g$ of $Gd^{3+}$ in both crystals were detected in our experiments.

IV - Discussion

In order to discuss the results it is useful to have the values of the spin-lattice coefficients related to strain $G_i^{(n)}$ defined in Eqs. 3 rather than the $C_i^{(n)}$. Since the elastic constants at the position of the impurity are not known it is necessary to assume that they are not much different than those of the bulk crystal and to use these values. The elastic constants of $ThO_2$ have been measured by Macedo et al.[15] at room temperature but no data seems to exist for $CeO_2$ neither for their temperature variation in both crystals; using these values[15] we calculated the spin lattice coefficients related to strain for $Gd^{3+}$ in $ThO_2$ at room temperature which are given in Table II.

Second order spin-lattice coefficients

There is not a general theory which could explain the values of these coefficients; the mechanism proposed by Blume and Orbach[6] for $Mn^{2+}$ in MgO which gave some agreement in the explanation of the trigonal coefficient $G_{5g}^{(2)}$ of $Gd^{3+}$ in $CaF_2$[7] cannot be applied to the study of $Gd^{3+}$ in $ThO_2$ and $CeO_2$ because optical data for $Gd^{3+}$ in these lattices do not exist. However it is interesting to note that the values of $G_{3g}^{(2)}$ and $G_{5g}^{(2)}$ are notably different for $Gd^{3+}$ in $ThO_2$ and $CeO_2$; this fact is surprissing in view of the similarity between these isomorphous lattices (the lattice parameter is $a = 5.411$ Å for $CeO_2$ and $5.600$ Å for $ThO_2$). It is very unprobable that the elastic constants of $CeO_2$ would be much different than those for $ThO_2$ and we dont know how to explain the differences observed in Table I and Figs. 3 and 4. Then it remains to be explained the values of the second

order spin-lattice coefficients and also the large differences between its values for $Gd^{3+}$ in $ThO_2$ and $CeO_2$.

Qualitative understanding of some of the mechanisms originating the spin lattice interaction could be obtained from the temperature variation of the spin-lattice coefficients shown in Figs. 3 and 4. The origin of this temperature variation of the second order spin-lattice coefficients will be analyzed in terms of implicit and explicit contributions[9]. Explicit contributions are a consequence of the lattice vibrations: the crystalline electric field is modulated by the phonons and gives an additional fluctuating interaction with the ion which has a temperature dependent thermal average. Explicit contributions to the spin Hamiltonian of the S-state ions have been studied for the fine and hyperfine structure parameters. Pfister et al.[16] and Serway[17] measured a temperature dependence of the D and E spin Hamiltonian parameters which cannot be explained as due to the thermal expansion of the crystal (in the case of $Mn^{2+}$ in $CaCO_3$, Serway[17] was able to substract a small implicit contribution to the change of D with temperature using the hydrostatic stress data reported by Wait[18]). Both authors explained their data in terms of a second order relativistic contribution proposed by Wybourne[1, 19] for $Gd^{3+}$ and applied later by Van Heuvelen[20] to the case of $Mn^{2+}$. Vibrational contributions to the hyperfine structure parameter have been considered by several authors[9,21-25]. A theory proposed by Simanek and Orbach[21] for $Mn^{2+}$ gives qualitative agreement with the experimental data and have been extended to rare earth S-state ions[22-24]. Data on the temperature variation of the hyperfine constant of the isotope 155 of $Gd^{3+}$ in $ThO_2$ have been reported by one of us[25] and explained with this theory.

Implicit contributions could arise from the thermal expansion of the crystal and from the change with temperature of the elastic constants. The variations of the lattice parameter due to the thermal expansion changes the electric field induced by the deformation of the crystal and then could produce a change of the spin-lattice coefficients. In order to measure directly the effect of the thermal expansion it would be necessary to perform an experiment where the spin-lattice coefficients were measured as a function of the lattice parameter but such uniaxial-hydrostatic stress experiments are out of our possibilities.

The large changes with temperature and the change of sign of $C_{5g}^{(2)}$ in $CeO_2$ when the temperature is varied could only be explained if the values of the coefficients are determined by the difference of two compiting contributions of opposite signs; small changes of these contributions due to the thermal expansion of the crystal could produce large changes of their difference. However this possibility seem unreasonable in view of the similarity of the amount of change of each coefficient in the $ThO_2$ and $CeO_2$ lattices even when their values are so different in the two crystals. Because of the absence of experimental information on the temperature variation of the elastic constants of $ThO_2$ and $CeO_2$ we can not estimate the contribution of this effect to the temperature variation of the spin-lattice coefficients. However in view of the data existing for other cubic crystals and the observed variation with temperature of the Young modulus of $ThO_2$ [26], they could introduce contributions to the changes of the coefficients smaller than 5% and there will be some contribution only for $C_{3g}^{(2)}$ measured in the $CeO_2$ crystal. In this case about one third of the measured temperature dependence could by justified by the changes of the elastic constants with temperature

and if this contribution is substracted the slope of the curve would be the same than that for $C_{3g}^{(2)}$ of $Gd^{3+}$ in $ThO_2$.

We conclude then that the temperature variation of the second order spin-lattice coefficients reported in this work is due to explicit effects derived from the coupling of the ion with the lattice vibrations. The temperature variation of a parameter C due to the coupling of the ion with the crystal vibrations trough the orbit-lattice interaction could be written as:

$$C\ (T) = C\ (RL) + C' \quad < \varepsilon^2 > \qquad (5)$$

where C (RL) is the value of C for a rigid lattice, $< \varepsilon^2 >$ is the thermal average over different normal modes of the square of the vibration amplitude and C' depends on the strength of the interaction.

Several approach could be taken for the calculation of $< \varepsilon^2 >$, probably the simplest is to suppose a single frequency Einstein model for the vibrations of the crystal as considered by Walsh et al.[9], Pfister et al.[16] and Serway[17]. A Debye model have been used in the calculation of $< \varepsilon^2 >$ by Simanek and Orbach[21] in the long wavelength limit and by Menne[24] without this restriction. If we assume that the coupling of the ion with the lattice vibrations involves mechanisms inside the $f^7$ configuration, only even symmetry modes of the cube of oxygen ligands would contribute to $< \varepsilon^2 >$. In the cases of $ThO_2$ and $CeO_2$ there are factors of 15 and 9 between the masses of the metal ions and the oxygens and to assume an Einstein model for the vibrations of the oxygens is a good approximation[29]. Then Eq. (5) can be written[9]

$$C\ (T) = C\ (RL) + K \coth \frac{\hbar \omega}{2kT} \qquad (6)$$

where $\omega$ is the assumed single vibrational frequency of the oxygens and K a numerical constant. Using a least square analysis we obtained a good fit of our experimental data with Eq. (6) supposing $\omega = 1 \times 10^{13}$ sec $^{-1}$. This value of $\omega$ is reasonable in view of the values reported by Willis[27] and Ali and Nagels[28]. The values of the spin-lattice coefficients corresponding to a rigid lattice C (RL) and the constant K which depends on its temperature variation for $Gd^{3+}$ in $ThO_2$ and $CeO_2$ are given in Table III.

Fourth order spin-lattice coefficients

Since no temperature variation have been observed for the fourth order spin-lattice coefficients of $Gd^{3+}$ in $ThO_2$ and $CeO_2$ we give only the values obtained at 290°K in Tables I and II. The values measured at other temperatures are inside of the experimental errors.

The strain coefficient related to a hydrostatic deformation, $G_{1g}^{(4)}$, gives the variation of the cubic field parameter with the lattice parameter a. From Eq. (2)

$$G_{1g}^{(4)} = \frac{a}{3} \frac{dB_4}{da} \qquad (7)$$

where $B_4$ is the cubic field parameter. It have been measured by Hurren et al.[29] for $Eu^{2+}$ (isoelectronic with $Gd^{3}$) in $CaF_2$, $SrF_2$ and $BaF_2$ in hydrostatic stress experiments. Our value of $G_{1g}^{(4)}$ for $Gd^{3+}$ in $ThO_2$ has the same magnitude than what is obtained from their data using Eq. (7).

It is interesting to note that the positive sign obtained for $G_{1g}^{(4)}$ indicate that the cubic field parameter $B_4$ decrease when the lattice parameter is increased, as expected from a simple point charge model for the crystalline field. However this is in apparent contradiction with the fact that $B_4$ increase by going from $ThO_2$ to $CeO_2$ when the lattice

parameter increases[3,11]. Probably lattice distorsions around the paramagnetic ion produce this anormal behaviour.

Data on the temperature dependence of $B_4$ for $Gd^{3+}$ in $ThO_2$ have been reported by Marshall[30] and Abraham and Boatner[31]. From Marshall's data we found:

$$\frac{d B_4}{dT} = \frac{1}{60} \frac{d b_4}{dT} = 1.25 \times 10^{-8} \text{ cm}^{-1}/°K \qquad (8)$$

The contribution from the thermal expansion to this temperature variation (implicit contribution) is

$$\left( \frac{d B_4}{dT} \right)_{\text{impl.}} = 3 \alpha G_{1g}^{(4)} \qquad (9)$$

where $\alpha$ is the linear expansion coefficient. From our value of $G_{1g}^{(4)}$ for $Gd^{3+}$ in $ThO_2$ and the value $\alpha$ (298°K) = $0.843 \times 10^{-5} \frac{1}{°K}$ given by Hoch and Momin[32] it is found:

$$\left( \frac{d B_4}{dT} \right)_{\text{impl.}} = 1.03 \times 10^{-8} \frac{\text{cm}^{-1}}{°K} \qquad (10)$$

The difference between the values given in Eqs. (8) and (10) is within the errors of the values involved in the estimation and it is concluded that the temperature variation of the cubic field parameter of $Gd^{3+}$ is due to implicit contributions coming from the thermal expansion of the crystal. No other conclusion can be made at this moment about the values of the fourth order spin lattice coefficients and remains for future theoretical work an explanation of the mechanisms contributing to these values.

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Table I - Values of the second and fourth order spin-lattice coefficients related to stress of $Gd^{3+}$ in $ThO_2$ and $CeO_2$ measured at 290°K.

Units of $\frac{cm}{dyne}$

| | $C_{3g}^{(2)} \times 10^{14}$ | $C_{5g}^{(2)} \times 10^{14}$ | $C_{1g}^{(4)} \times 10^{16}$ | $C_{3g}^{(4)} \times 10^{16}$ | $C_{5g}^{(4)} \times 10^{16}$ |
|---|---|---|---|---|---|
| $ThO_2$ | (- 1.11 ± 0.06) | (- 6.35 ± 0.10) | (0.70 ± 0.05) | (- 1.2 ± 0.2) | (5.0 ± 0.7) |
| $CeO_2$ | (- 8.7 ± 0.2) | (1.0 ± 0.2) | (0.80 ± 0.07) | (- 1.0 ± 0.3) | (6.5 ± 0.7) |

Table II - Values of the second and fourth order spin lattice coefficients related to strain of $Gd^{3+}$ in $ThO_2$ measured at 290°K. Units of $cm^{-1}$

$$G_{3g}^{(2)} = (-2.9 \pm 0.2) \times 10^{-2} \qquad G_{5g}^{(2)} = (-5.1 \pm 0.1) \times 10^{-2}$$

$$G_{1g}^{(4)} = (4.1 \pm 0.3) \times 10^{-4} \qquad G_{3g}^{(4)} = (-3.1 \pm 0.6)\ 10^{-4} \qquad G_{5g}^{(4)} = (4.0 \pm 0.6)\ 10^{-4}$$

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Table III - Values of the constants $C_{3g}^{(2)}(RL)$, $C_{5g}^{(2)}(RL)$, $K_{3g}^{(2)}$ and $K_{5g}^{(2)}$ obtained by a least square fit of the experimental data with Eq. ( for $\omega = 1 \times 10^{13}$ $sec^{-1}$, $C_{3g}^{(2)}(RL)$ and $C_{5g}^{(2)}(RL)$ are in units of $10^{-14}$ cm/dyne.

| | $C_{3g}^{(2)}$ (RL) | $K_{3g}^{(2)}$ | $C_{5g}^{(2)}$ (RL) | $K_{5g}^{(2)}$ |
|---|---|---|---|---|
| $ThO_2$ | - 0.51 ± 0.02 | - 0.079 ± 0.003 | - 9.25 ± 0.10 | 0.38 ± 0.01 |
| $CeO_2$ | - 7.50 ± 0.03 | - 0.153 ± 0.005 | - 1.21 ± 0.03 | 0.292± 0.005 |

Figure captions

Fig. 1 - Shifts of the EPR lines of $ThO_2 : Gd^{3+}$ for P// $[1\bar{1}0]$ and $H_o$ // $[001]$ corresponding to a compression of P = 1 dyne/cm$^2$ at 290°K;

a) experimental shifts,

b) second order tetragonal contribution,

c) fourth order hydrostatic contribution,

d) fourth order tetragonal contribution,

e) total calculated shifts.

The shifts were calculated with the values of the spin lattice coefficients given in Table I and are in units of $10^{-14}$ cm$^{-1}$.

Fig. 2 - Shifts of the EPR lines of $ThO_2 : Gd^{3+}$ for P// $[1\bar{1}0]$ and $H_o$// $[\bar{1}11]$ corresponding to a compression of P = 1 dyne/cm$^2$ at 290°K;

a) experimental shifts

b) second order trigonal contribution,

c) fourth order hydrostatic contribution,

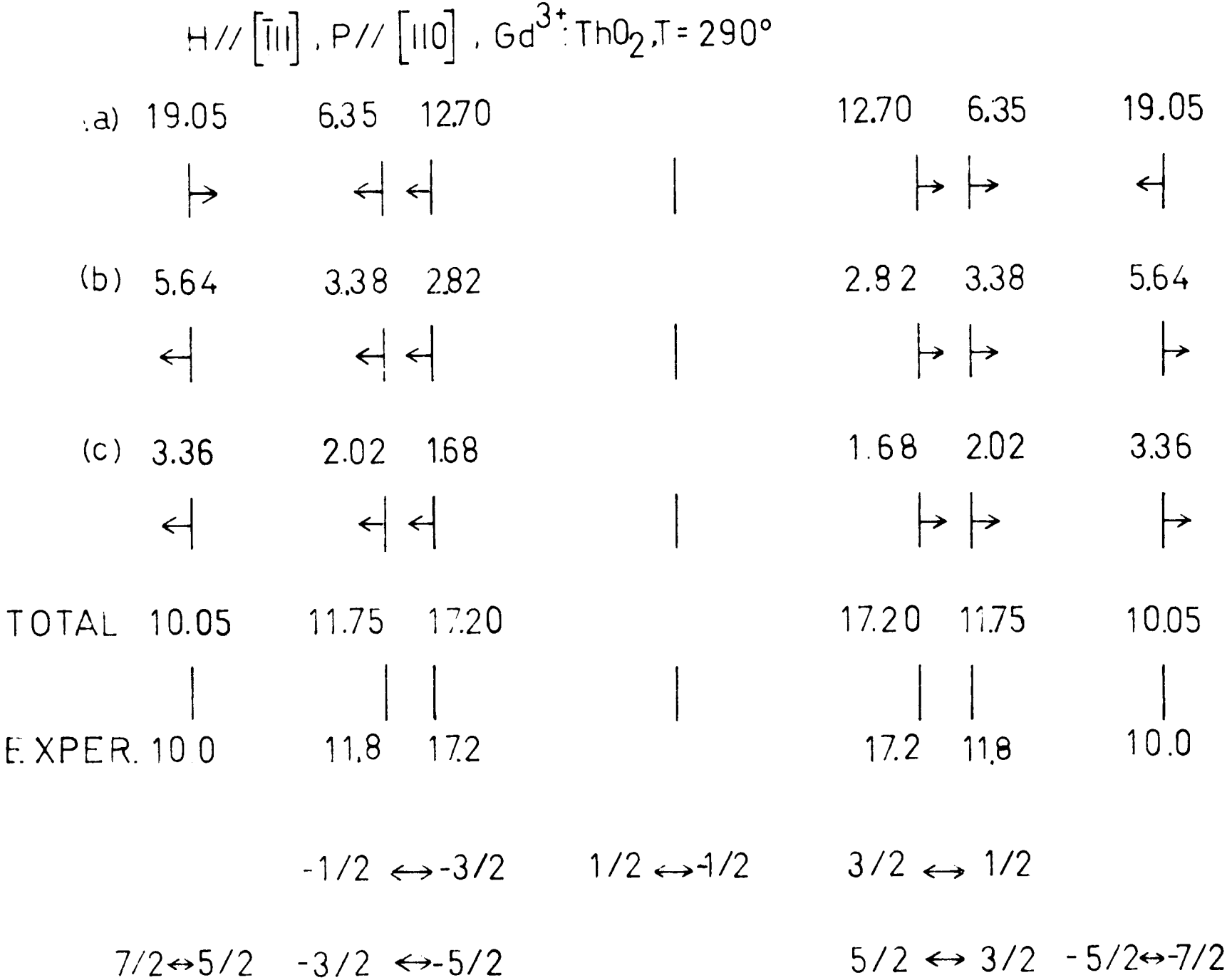
d) fourth order trigonal contribution,

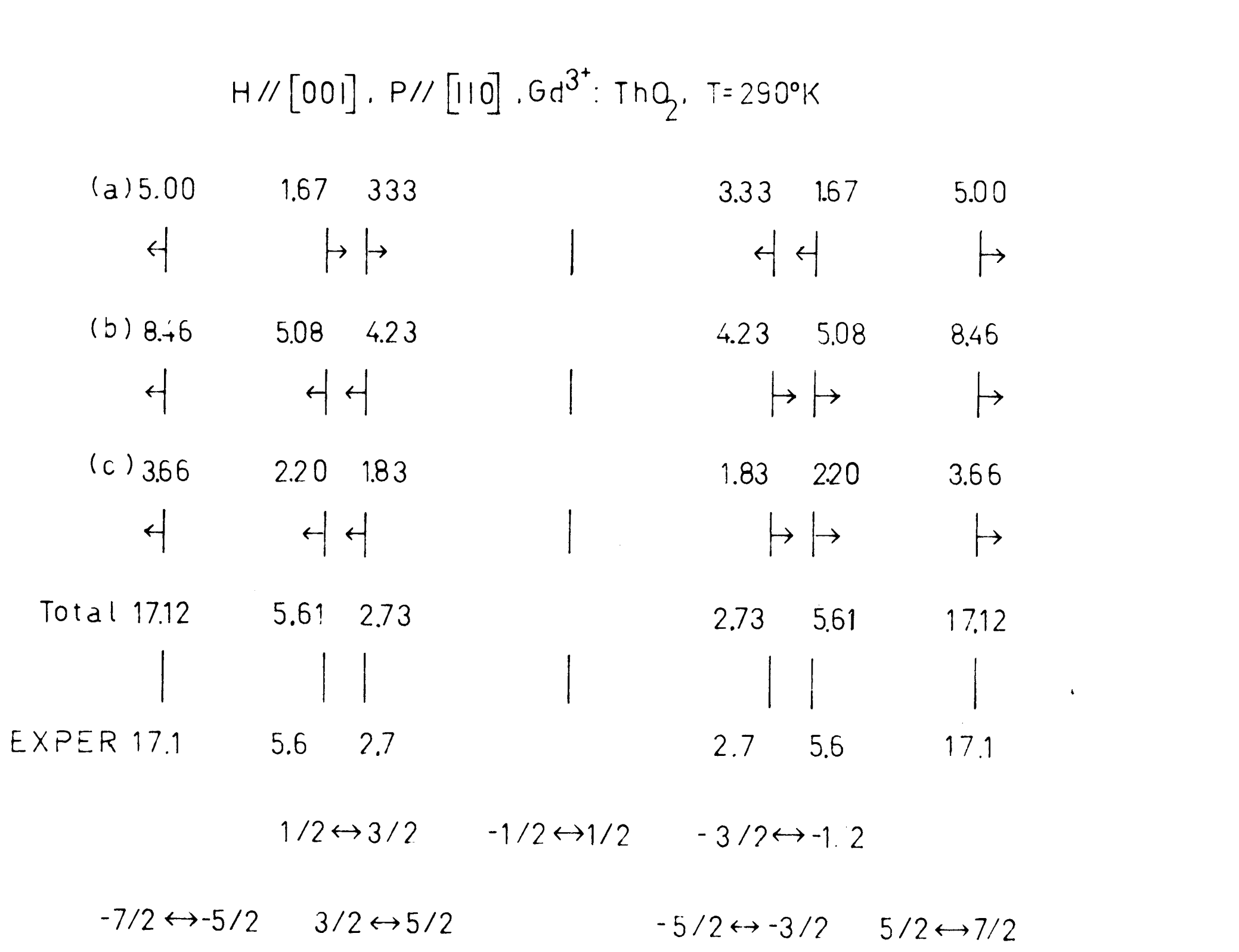
e) total calculated shifts.

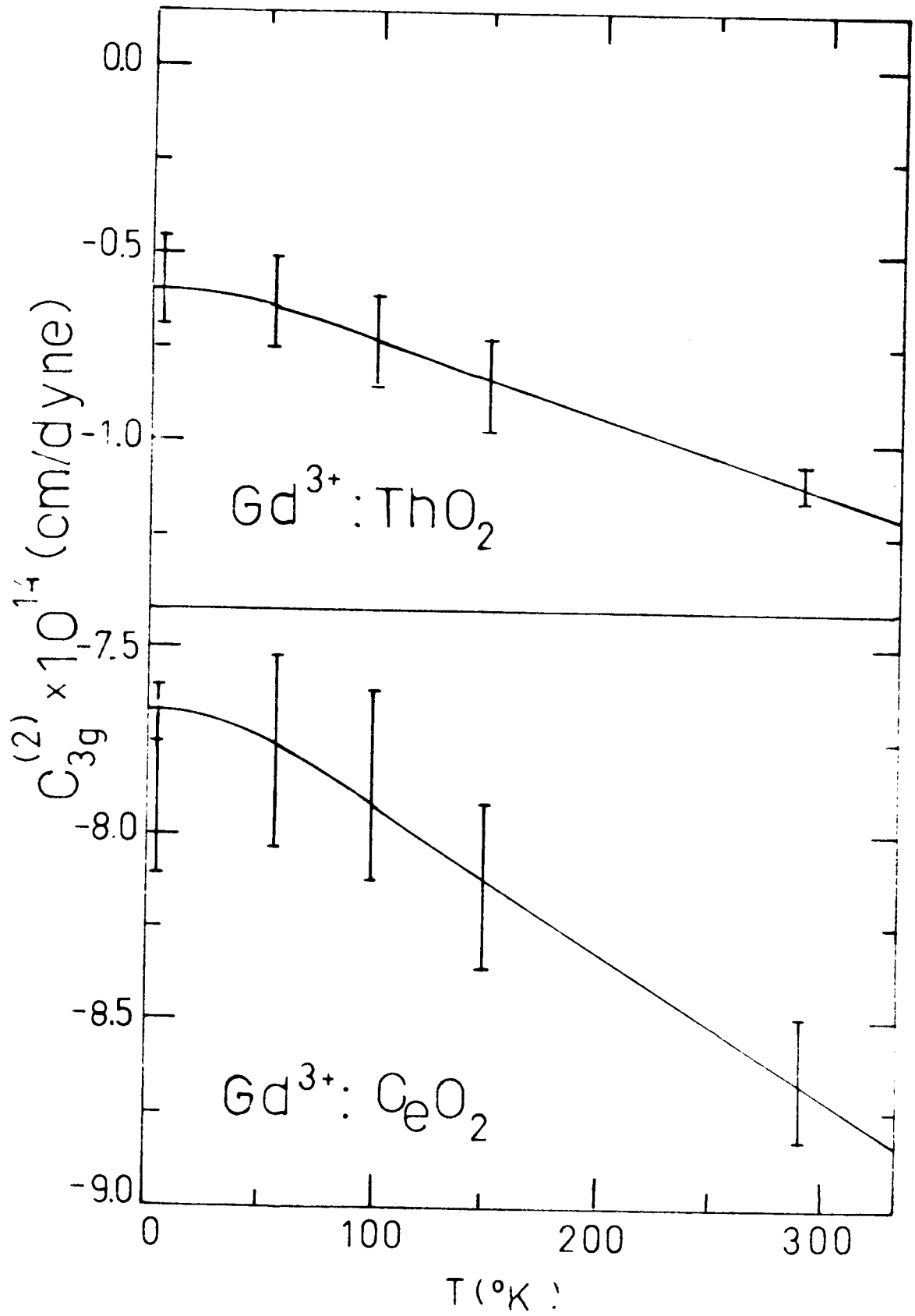
The shifts were calculated with the values of the spin-lattice coefficients given in Table I and are in units of $10^{-14}$ cm$^{-1}$.

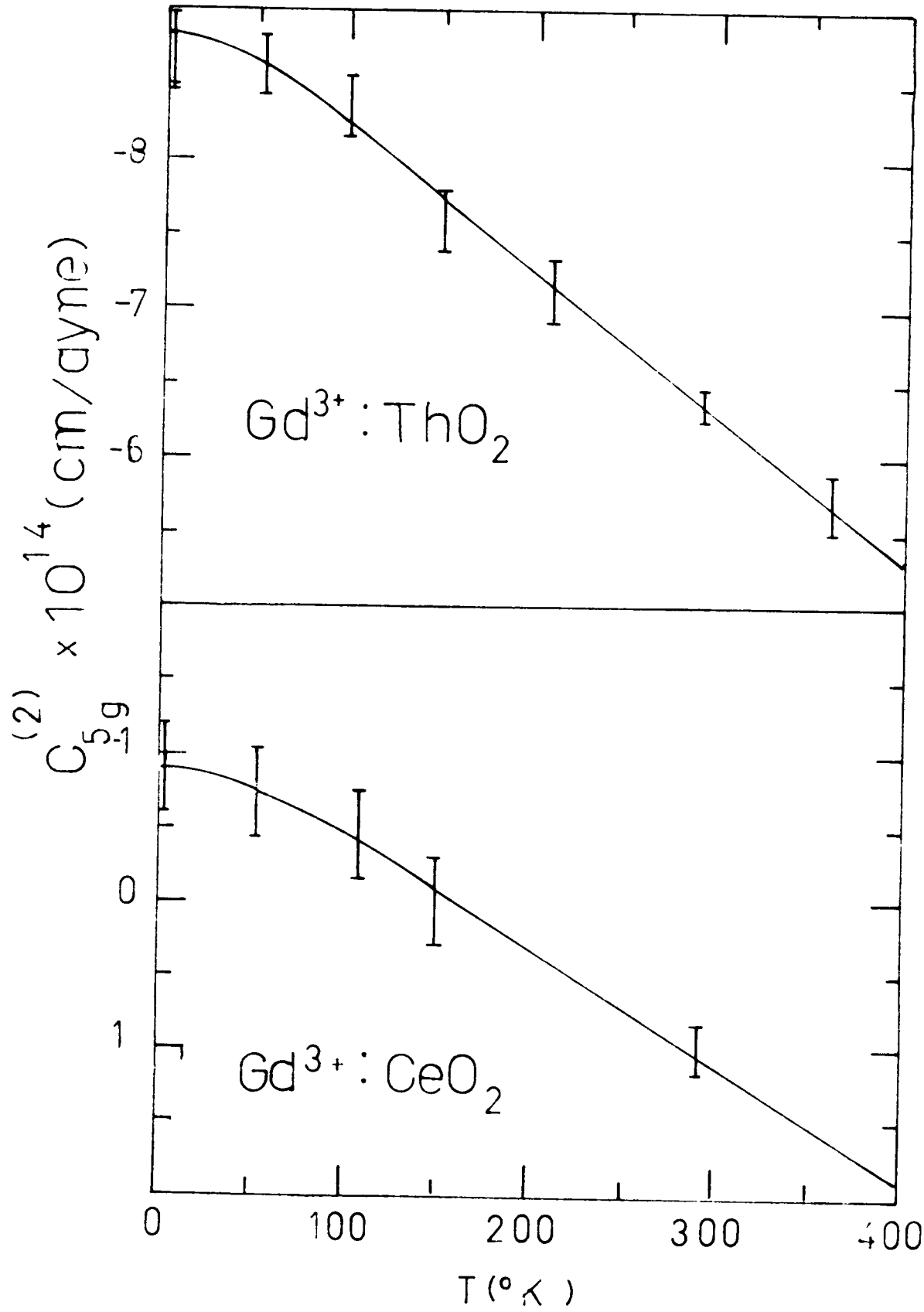
Fig. 3 - Temperature dependence of the second order tetragonal spin-lattice coefficient $C_{3g}^{(2)}$ of $Gd^{3+}$ in $ThO_2$ and $CeO_2$.

Fig. 4 - Temperature dependence of the second order trigonal spin lattice coefficient $C_{5g}^{(2)}$ of $Gd^{3+}$ in $ThO_2$ and $CeO_2$.


H // [1̄11] , P // [110] , $Gd^{3+}$ : $ThO_2$ , T = 290°
(a) 19.05 6.35 12.70 12.70 6.35 19.05
(b) 5.64 3.38 2.82 2.82 3.38 5.64
(c) 3.36 2.02 1.68 1.68 2.02 3.36
TOTAL 10.05 11.75 17.20 17.20 11.75 10.05
EXPER. 10.0 11.8 17.2 17.2 11.8 10.0
-1/2 ↔ -3/2
1/2 ↔ -1/2
3/2 ↔ 1/2
7/2 ↔ 5/2
-3/2 ↔ -5/2
5/2 ↔ 3/2
-5/2 ↔ -7/2


H // [001] . P // [110] . $Gd^{3+}$ : $ThO_2$ . T = 290°K
(a) 5.00
1.67
3.33
3.33
1.67
5.00
(b) 8.46
5.08
4.23
4.23
5.08
8.46
(c) 3.66
2.20
1.83
1.83
2.20
3.66
Total 17.12
5.61
2.73
2.73
5.61
17.12
EXPER 17.1
5.6
2.7
2.7
5.6
17.1
1/2 ↔ 3/2
-1/2 ↔ 1/2
-3/2 ↔ -1/2
-7/2 ↔ -5/2
3/2 ↔ 5/2
-5/2 ↔ -3/2
5/2 ↔ 7/2


0.0
-0.5
-1.0
-7.5
-8.0
-8.5
-9.0
$C_{3g}^{(2)} \times 10^{14}$ (cm/dyne)
$Gd^{3+}:ThO_2$
$Gd^{3+}:CeO_2$
0
100
200
300
T (°K)


-8
-7
-6
$Gd^{3+}:ThO_2$
$C^{(2)}_{5g}$ $\times 10^{14}$ (cm/dyne)
-1
0
1
$Gd^{3+}:CeO_2$
0
100
200
300
400
T(°K)