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# Bulk and local elastic relaxation around optically excited centers

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The macroscopic refractive effect arising from an optically excited $Cr^{3+}$ center in a Gd-Sc-Ga garnet crystal was observed and measured using time-resolved beam-deflection spectroscopy. The excited-state effect is much larger than the thermal effect. The predominant mechanism is concluded to be the refractive effect stemming from the elastic dilation of the $CrO_6$ cluster in the excited $^4T_2$ state of $Cr^{3+}$. The bulk expansion per excited ion is $\approx 12$ Å$^3$. An expansion of $\approx 0.13$ Å of the oxygen coordination sphere is derived in the approximation of an isotropic elastic continuum and a fully symmetric dilation. This displacement is in agreement with the optical spectra in the framework of the configuration coordinate model.

## INTRODUCTION

The majority of dynamical processes of excited centers in solids involve the interaction of the electronic state with the phonon bath or with local vibrations. The configuration coordinate diagram model[1] used in the following considerations is one of the most useful conceptual aids in understanding the interactions of such centers with the elastic lattice. Despite its simplicity it provides an efficient description of optical spectra and of relaxation processes. The model is based on the assumption, that all degrees of freedom in vibronic motion can be approximated by only a few "quasimolecular" normal coordinates $Q_i$ of the center and its coordination sphere. The electronic plus elastic energy is, in harmonic approximation, a quadratic function of the coordinates $Q_i$. The equilibrium coordinates in the excited state $Q_{ei}$ generally differ from that in the ground state $Q_{gi}$. Consequently, the relaxation in the excited state is accompanied by an elastic distortion of the surrounding lattice. Conclusions about changes in the equilibrium coordinate $\delta Q_i = Q_{ei} - Q_{gi}$ in the relaxed excited state can be drawn from the spectral band shape in absorption and emission.[2] Such an analysis involves the examination of Franck-Condon factors using effective vibration frequencies and force constants. A detailed analysis also requires the consideration of bulk phonon spectra.[3]

A direct measurement of the lattice changes caused by an excited state was achieved by Pruss and Danielmayer.[4] In the stoichiometric $CeP_5O_{14}$, which is a particularly suitable material for such an investigation, a large fraction of the $Ce^{3+}$ ions was excited by a high-energy pulse of a XeCl excimer laser. The subsequent changes of the lattice were observed by time-resolved x-ray diffraction using x-ray pulses from the Deutsches Elektronen-Synchrotron (DESY) synchotron source. An excited-state effect on the lattice constant was measured and identified. Such experiments are very difficult and barely feasible even with the most suitable material, one of the problems being the distinction of the excited state effect from the inevitable thermal expansion.

In this paper I present and discuss a simple optical method which is suitable to investigate the macroscopic effect of an optically excited ion on the elastic host lattice. The observed excited-state effect is related to the local displacements around the center. The experimental technique used is time-resolved beam deflection, which is a detection variant of thermal-lensing laser spectroscopy.[5] The change in the refractive index ($n$) of a sample following pulsed excitation is measured by means of the deflection of a probe beam caused by the induced thermal lens. We have previously utilized the same technique to identify and measure the refractive effect of the solvent cage relaxation around an excited transition metal ion complex in liquid water.[6] Here, this technique is extended to a transition metal ion center in a solid. It is used to determine the change in macroscopic mass density per excited $Cr^{3+}$ ion in the cubic crystal Gd-Sc-Ga garnet [$Gd_3Sc_2(GaO_4)_3$, GSGG].

## EXPERIMENTAL DETAILS

Experiments were carried out as previously described.[6] The $^4T_2$ state of $Cr^{3+}$ was excited using a $Q$ switched, frequency doubled Nd:YAG laser, or a dye laser at 650 nm. The lasers were operated close to the Gaussian transverse-electromagnetic ($TEM_{000}$) mode. In the experiments discussed here the $1/e$ beam radius ($\sigma$) in the sample was adjusted to 150 $\mu$m. The pulse energy in the experiments was kept below 30 $\mu$J (a fluence of 42 mJ/cm$^2$) to exclude excited-state absorption. The time dependence of the refractive change was probed by a HeNe laser beam propagating collinear to the pump beam, i.e., all refractive changes discussed refer to 632 nm. The probe beam radius was 25 $\mu$m in the probe volume. The Rayleigh lengths of both beams were larger than the thickness (1.5 mm) of the sample. The beams were combined and separated using dichroic mirrors. The deflection of the probe beam by the sample is proportional to the gradient of the bulk refractive index $\mathrm{grad}_r(n)$. For a Gaussian pump beam profile it is also proportional to the index change ($\delta n$). The probe beam deflection was measured by a quadrant photodiode and a differential amplifier and recorded by an averaging transient digitizer. The time resolution is limited to about 0.5 $\mu$s by the speed of sound which determines the macroscopic elastic response.[5]

GSGG:Cr$^{3+}$ was chosen for this investigation because its optical and fluorescence properties are well characterized[7,8] and the thermomechanical data have been determined.[9] The optical spectroscopy is determined by the Cr$^{3+}$ centers. The cubic crystal-field strength $Dq$ is relatively low and the splitting of the $^4T_2$ and $^2E$ excited states is smaller than the thermal energy at room temperature.[10] The $^4T_2$ and $^2E$ occupation is therefore given by their degeneracies.[8] GSGG has cubic symmetry, although the crystal structure is quite complicated[11] with eight formula units in the unit cell. In GSGG, the Cr$^{3+}$ ion substitutes for Sc$^{3+}$ on octahedral sites with oxygen coordination.[10] These are not regular octahedra but they are distorted along a threefold axis and twisted about the [101] direction giving a point symmetry $C_{3h}$ and eight inequivalent sites. The main spectroscopic features of the Cr$^{3+}$ center, however, can be well described in cubic approximation[10] despite this lower symmetry. The cubic approximation also suffices for the experiments considered here, because the elastic response is determined by the cubic space group, all sites are equally excited and the experiment detects the average, macroscopic refractive effect. Thermal lensing of a garnet on a time scale of seconds has been previously reported.[12]

## EXPERIMENTAL RESULTS

The photo-refractive effect of GSGG:Cr$^{3+}$ after pulsed excitation at 650 nm is depicted in Fig. 1. A purely *thermal* signal would be composed of a steplike response to the prompt heat released in the intra-$^4T_2$ relaxation and a further, exponential increase from the delayed heat released in the $^4T_2$-$^4A$ relaxation (Fig. 2). The actually observed time dependence is very different (Fig. 1). The signal reversal following a fast response clearly shows refractive contributions of *nonthermal* origin. The decrease is almost exponential with a time constant matching the observed fluorescence lifetime (112 $\mu$s). This agreement reveals that the effect is caused by the excited-state population. This conclusion was confirmed by measurements of other crystals with low-field Cr$^{3+}$ sites and different excited state lifetimes where the nonthermal refraction was always found to be proportional to the excited-state population.

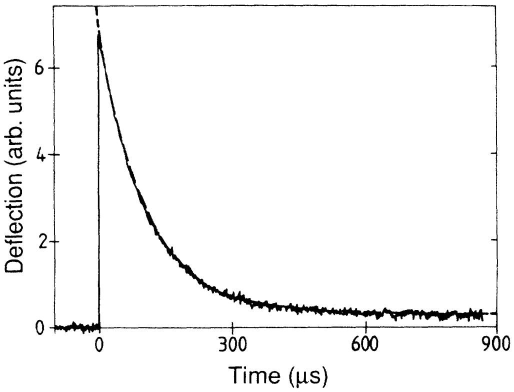

FIG. 1. Refractive response of GSGG:Cr$^{3+}$ to a pulsed excitation at 650 nm. The dashed line is a fit by a superposition of the excited-state effect and of the thermal effect including thermal diffusion.

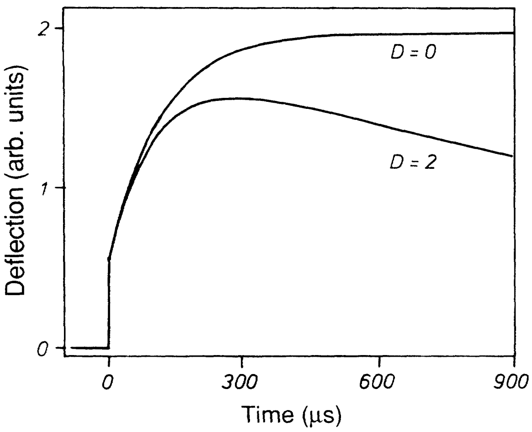

FIG. 2. Purely thermal refractive response showing prompt and delayed heat release. The upper trace is without heat diffusion, the lower with the thermal diffusivity $D = 0.02$ cm$^2$/s of GSGG. The pump pulse profile and the probe distance are as described in the text.

## PHOTOREFRACTIVE EFFECT IN GSGG:Cr$^{3+}$

The experiments show refractive effects of thermal and of excited-state origin. The change in the index of refraction $n$ can be written as

$$\delta n = \left[\frac{\partial n}{\partial T}\right]_V dT + \left[\frac{\partial n}{\partial \rho}\right]_P d\rho + \left[\frac{\partial n}{\partial c}\right] dc \ , \qquad (1)$$

where $T$ is the temperature, $\rho$ the mass density and $c$ the excited-state density. The constant-volume ($V$) term, which accounts for thermal changes in the population of electronic states, can be neglected in an insulator. The constant-pressure ($P$) term describes the effect of thermal expansion by the heat released in the excited-state relaxation. The thermal strain varies the refractive index via the elasto-optic effect. The excited-state term also may be separated in an isobaric and an isochoric contribution. At constant pressure the lattice relaxes elastically around the excited ion and the strain again causes an elasto-optic effect. The constant volume part is from the changes in electronic resonances when exciting a Cr$^{3+}$ ion in the $^4T_2$ state. In the oscillator model of the index of refraction[13] the contribution $\delta n_i$ of $N_i$ centers in the state $i$ is given by

$$\delta n_i(\omega) = \left[\frac{N_i e^2}{2m\epsilon_0}\right] \sum_k \frac{f_{ik}}{\omega_{ik}^2 - \omega^2} \ , \qquad (2)$$

where $\omega$ is the light frequency, $e$ is the electron charge and $m$ its mass, $\epsilon_0$ is the dielectric constant and $\omega_{ik}$ and

$f_{ik}$ are the resonance frequency and the oscillator strength of the transition from the state $i$ to the state $k$, respectively. For the changes considered here the $f_{ik}$ for the optically allowed transitions from the $(3d)^3$ crystal-field states of $Cr^{3+}$ to the charge-transfer states at about 30 000 $cm^{-1}$ (Ref. 14) are the main contributions to (2). Their Einstein coefficients $B_{ik}$ are expected to be about the same and, because $f_{ik}=B_{ik}\omega_{ik}$, the $f_{ik}$'s decrease linearly with $\omega_{ik}$.[13] A refractive effect would arise because of the nearly quadratic reduction of the resonance energy denominators for ions in the $^4T_2$ excited state as compared to the $^4A$ ground state. This electronic resonance effect would increase the refractive index, in agreement with the experimental observations. They show an increase by the excited state because it has the same sign as the thermal effect which is positive in GSGG.[15] However, the electronic resonance effect is evidently considerably smaller than the elastic relaxation effect. In $Al_2O_3:Cr^{3+}$ (ruby) which has about the same positive thermo-optical coefficient[16] no comparable excited-state refractive effect was observed because the first excited state ($^2E$) does not couple to the lattice. For a $Mn^{2+}$ center which contracts in the first excited state we could show unambiguously that the elastic effect is by far larger than the electronic resonance effect.[6] Therefore the electronic resonance effect on the refractive index may be assumed to be negligible in the following consideration. With these approximations the refractive changes reduce to strain effects from the thermal expansion and from the elastic deformation by the excited state. This can be conveniently written in terms of the mass density changes:

$$\delta n \cong \left[\frac{\partial n}{\partial \rho}\right]\left[\left[\frac{\partial \rho}{\partial T}\right]dT+\left[\frac{\partial \rho}{\partial c}\right]dc\right] . \tag{3}$$

The two terms have a distinguishable time dependence. The lattice relaxation decays exponentially like the excited state while the thermal effect accumulates all the heat released and decreases much slower by the diffusive decay of the thermal lens. This difference is used in the following analysis to infer quantitatively the elastic expansion of the lattice by the excited ions.

## CORRECTION OF HEAT DIFFUSION

The $^4T_2$ lifetime in GSGG is relatively long and the decrease of the signal due to the diffusive decay of the thermal lens has to be considered for the analysis. The solution $T(r,t)$ of the heat diffusion equation for a pulsed, linelike heat source of Gaussian profile is given by[17]

$$T(r,t) \propto \frac{1}{(\sigma^2+4Dt)}\exp\left[-\frac{r^2}{(\sigma^2+4Dt)}\right] , \tag{4}$$

where $r$ is the radius, $t$ the time after the pulse and $D$ is the thermal diffusivity. The beam deflection signal $s(r,t)$ as measured in the experiments is proportional to $\mathrm{grad}_r(T)$ for the thermal effect:

$$s(r,t) \propto \frac{r}{(\sigma^2+4Dt)^2}\exp\left[-\frac{r^2}{(\sigma^2+4Dt)}\right] . \tag{5}$$

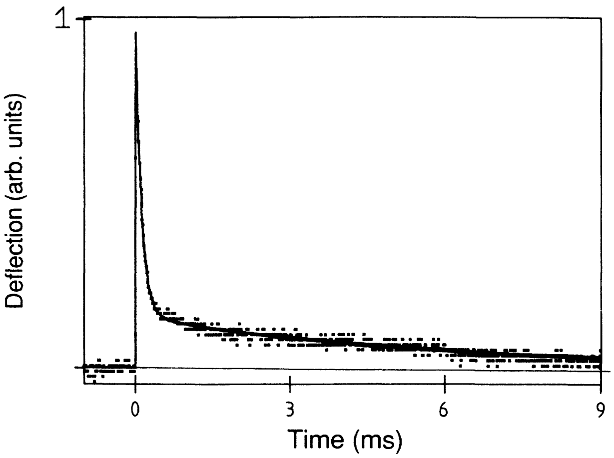

FIG. 3. Deflection signal of $GSGG:Cr^{3+}$ including part of the diffusive decay of the thermal lens. Excitation was at 532 nm in order to increase the thermal effect. The solid line is a fit of the data using a thermal diffusivity $D=0.02$ $cm^2/s$ and including the additional exponential decay of the excited-state refractive effect.

Figure 3 depicts the refractive response on a time scale long enough to show both the excited-state effect and the diffusive decay of the thermal lens. The latter is in quantitative agreement with Eq. (5). In particular, the diffusivity $D=2$ $mm^2/s$ determined from the data was found to confirm the value $D=2.1$ $mm^2/s$ calculated using the thermal data.[9] Most of the heat is released within the fluorescence lifetime $\tau=115$ $\mu s$. With the pump beam profile used in the experiments ($\sigma\cong150$ $\mu m$) the thermal lens is almost stationary during that time ($\sigma^2 \gg 4D\tau$) and the delayed heat from the $^4T_2$ decay just increases the amplitude of the lens.

## THE REFRACTIVE EFFECT OF THE $^4T_2$ STATE

Equation (3) can be used to infer from the measurements the bulk expansion of GSGG caused by an elastically relaxed $^4T_2$ state without the need to separately calibrate the deflection signal with respect to the refractive index gradient. Immediately after the pump pulse the signal amplitude arises from the elastic relaxation and the prompt heat, while only the effect of the total heat remains after the $^4T_2$ decay (Fig. 1). The ratio of the excited-state effect to the thermal effect is obtained from the two signal amplitudes. It is expected to be independent of the excitation density because in a linear system each excited ion releases the same amount of heat and causes the same elastic distortion. The amount of heat deposited in the probe volume is calculated from the spectroscopic data. Note that the energy carried off by the acoustic wave can be neglected. For the excitation at 650 nm, and given the 89% fluorescence quantum efficiency and the center of the fluorescence band at 770 nm,[7] 7.1% of the absorbed energy is released as prompt heat and 18.5% as delayed heat. At the excitation densities of the experiment the temperature increase in the detection volume is $2\times10^{-3}$ K per pump pulse. With

$\partial n/\partial T = 9\times10^{-6}$/K,[15] the solid signal in Fig. 1 corresponds to $dn/n = 2\times10^{-8}$. The subsequently induced local thermal expansion is calculated using the mass density $\rho$ (6.44 g/cm$^3$), the specific heat $C_p$ (0.4 J/g K) and the thermal volume expansion $\beta$ ($2.25\times10^{-5}$/K) of GSGG.[9] Each excited ion causes a total thermal expansion of $\delta V_{\text{th}} = 0.67$ Å$^3$. In the beam-deflection experiments, the prompt signal is 22.5 times larger than the purely thermal signal at 900 $\mu$s, see Fig. 1. The heat conversion would increase in the presence of excited-state absorption. However, it is negligible at the excitation density used[8] and no dependence of the factor on the pump pulse energy was found at the fluences used. In order to obtain from the experimental factor the amount of the bulk expansion by the excited-state relaxation it has to be taken into account that heat diffusion according to Eq. (4) decreased the thermal signal by approximately a factor of 0.61 and that heat contributes to the prompt signal (2%). Furthermore, only $\frac{3}{4}$ of the excited ions are in the $^4T_2$ state and do contribute to the elastic effect because $^4T_2$ and $^2E$ are nearly degenerate[8] and the vibrational coupling of $^2E$ is weak. It follows that the macroscopic lattice expansion $\delta V_e$ caused by the $^4T_2$ elastic relaxation is about 17 times larger than the thermal expansion. It amounts to about $\delta V_e \cong 12$ Å$^3$ and decreases the refractive index by $5\times10^{-24}$ per excited ion and unit volume.

## DILATION CENTER IN AN ELASTIC SOLID

The observed macroscopic volume change $\delta V_e$ is related to the local, microscopic displacements $\delta Q_i$ by the elastic properties of the solid.[18] The excited $\text{Cr}^{3+}$ ion is a substitutional defect. Near the defect the displacements should be described by lattice theory. However, they may be approximated using an isotropic elastic continuum because in a cubic crystal the differences to the lattice description are small[18] and the anisotropy parameter of GSGG is close to 1.[19] In a further approximation the excited ion is treated as a dilation center. Under these conditions the volume change close to the center is related to $\delta V_e$ by a factor of approximately $(1+\Gamma)$, with[18]

$$\Gamma = \frac{4C_{44}}{C_{11}+2C_{12}} , \tag{6}$$

where $C_{ik}$ are the elastic moduli. $\Gamma = 0.66$ is obtained from the $C_{ik}$ of GSGG.[9] A crude approximation of the nearest-neighbor displacements can be obtained by requiring that it leads to the inferred local volume change $\delta V_1 = \delta V_e/(1.66)$. The oxygen coordination sphere surrounding the chromium has a radius of 2.1 Å in the ground state.[11] From its volume and the local volume increase $\delta V_1$, a change of $\delta Q_1 \cong +0.12$ Å in the fully symmetric normal coordinate $Q_1$ in the excited state is calculated. The positive sign corresponds to an expansion of the oxygen octahedron in agreement with the elastic relaxation expected from the slope of the $^4T_2$ energy in the Tanabe-Sugano diagram.[20]

## DILATION AND VIBRONIC COUPLING

The local equilibrium change $\delta Q_1$ in the excited state has a simple relation to the vibrational frequency $\nu_1$ and to the vibronic coupling strength $S_1$ in the configuration-coordinate model with linear coupling of a single frequency.[21] Both are also related to the width and Stokes shift of the absorption and fluorescence bands. The dilation parameter inferred above is compatible with this model because all displacements have also been lumped together in a single effective $\delta Q_1$. The vibrational coupling strength expressed by the Huang-Rhys factor $S_1$ is given by

$$S_1 = (2\pi^2/h)\mu\nu_1(\delta Q_1)^2 , \tag{7}$$

where $\nu_1$ is the vibrational frequency, $\mu$ the effective mass of the normal mode and $h$ is Planck's constant. It follows from symmetry considerations and spectroscopic data that, in octahedral coordination, only the breathing mode $Q_1$ and the tetragonal mode $Q_3$ couple significantly to the $^4T_2$ state.[2] The coordinate $Q_1$ describes a fully symmetric dilation center. $Q_3$ corresponds to an axial displacement along one of the fourfold axis (Jahn-Teller mode). This component of distortion was not considered in the calculation of the local displacement because, in a cubic system, its macroscopic elastic effect cannot be distinguished from a dilation.[18] The approximation by an effective dilation seems justified because $Q_3$ changes the effective volume of the center much less than $Q_1$ and the macroscopic effect is expected to be small. The axial displacement and its elastic field which is related to a "double force tensor"[18] can possibly be separated in a suitable axial system.

To obtain the coupling factor $S_1$ from Eq. (7), the effective vibrational frequency $\nu_1$ of the $\text{CrO}_6$ cluster is needed. The best estimate would be derived from the fully symmetric components of the one-phonon density of states from which the $^4T_2$ phonon sideband is composed. Vibronic details have been analyzed for the $^2E$ sideband only[22,23] but not the $^4T_2$. The $^2E$ ($R$ line) sideband shows features up to 600 cm$^{-1}$ with strong maxima between 150 and 400 cm$^{-1}$ (Fig. 10 in Ref. 20). Vibrational features with energies around 400 cm$^{-1}$ are also discernible in the low-temperature $^4T_2$ fluorescence spectrum (Fig. 3 in Ref. 20). Andrews[15] obtained $\nu_1 = 365$ cm$^{-1}$ from a fit of all quartet absorption bands of GSGG:$\text{Cr}^{3+}$.

If the same effective vibrational frequency $\nu_1 = 365$ cm$^{-1}$ is assumed here, the Huang-Rhys parameter for the coupling strength of the mode $\nu_1$ according Eq. (4) is $S_1 = 2.7$, using the effective mass of the oxygen octahedron ($\mu = 96$ amu) and the dilation $\delta Q_1 \cong +0.12$ Å inferred above. This value happens to agree with the coupling factor for the normal coordinate $Q_1$ derived from a Frank-Condon analysis of high-resolution spectra of $\text{Cr}^{3+}$ in a compound with $D_{3d}$ symmetry.[24]

These parameters are not expected to fully describe the optical spectra within the configuration-coordinate model and a single mode $\nu_{\text{eff}}$. The Stokes shift $\nu_s$ between the maxima of the $^4T_2$ absorption and fluorescence band ($\nu_s = 2500$ cm$^{-1}$ in GSGG:$\text{Cr}^{3+}$) is given by

$\nu_s=(2S-1)\nu_{\text{eff}}$. For a given Stokes shift $\nu_s$ and displacement $\delta Q_1$ the dependence of $S$ on the frequency $\nu_1$ is different. The two values would agree for $\nu_{\text{eff}}=265\ \text{cm}^{-1}$ and $S=5.3$. Although $\nu_1$ is in the range estimated above, the coupling seems too strong. However, the Stokes shift of the ${}^4T_2$ stems not only from the fully symmetric mode $\nu_1$ but also from the tetragonal Jahn-Teller mode $\nu_3$. Consequently,

$$\nu_s=(2S_1-1)\nu_1+(2S_3-1)\nu_3\ ,$$

where $S_1$ and $S_3$ are the coupling factors for the symmetric and tetragonal mode, respectively, and $S=S_1+S_3$. The tetragonal displacement and coupling does not contribute to the refractive data. Provided about the same frequency $\nu=365\ \text{cm}^{-1}$ may be assumed for both modes, the coupling strength for both modes is about the same. This again is in agreement with the values derived for ${}^4T_2$ from high-resolution spectra of $\text{Cr}^{3+}$ in $D_{3h}$ sites.[24]

The consistency of the local elastic relaxation of the ${}^4T_2$ inferred from the refractive data with the one derived from the optical spectra, within the framework of the configuration coordinate model, confirms the approximations made in the elastic properties, i.e., the description by an elastic continuum and a dilation center.

## CONCLUSIONS

The results demonstrate that time-resolved beam-deflection spectroscopy is a simple technique to observe and measure the macroscopic refractive effect arising from an optically excited center in a solid. This technique is suitable for states with a lifetime longer than the elastic response time which is limited by the speed of sound. The excited state effect can be distinguished from the thermal effect by the differences in the time behavior. In GSGG:$\text{Cr}^{3+}$ the excited-state effect is much larger than the thermal effect because of the good fluorescence efficiency and the small Stokes shift. The predominant mechanism was identified as the refractive effect stemming from the bulk expansion caused by the elastic dilation of the $\text{CrO}_6$ cluster in the excited ${}^4T_2$ state of $\text{Cr}^{3+}$. This elastic relaxation is not unique to $\text{Cr}^{3+}$ but considerable in all states with strong vibronic coupling and is expected to be present in most optical centers with transition metal ions. An excited-state refractive effect may also arise from the change in electronic resonances involving transitions to charge-transfer states. Even though it was not ruled out experimentally, I argue from a comparison with other systems that it has to be considerably smaller than the elastic effect and is disregarded. The determined macroscopic expansion per excited ion is $\approx 12\ \text{Å}^3$. It is related to the microscopic displacements in the approximation of an isotropic elastic continuum and a dilation center. Axial distortions caused by the Jahn-Teller effect of the ${}^4T_2$ state are lumped together with the fully symmetric dilation. An expansion of $\approx 0.13$ Å of the oxygen coordination sphere is derived. This dilation is in agreement with the optical spectra in the framework of the configuration-coordinate model.

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