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Optical alignment of axial Fe centers in $KTaO_3$

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Axial Fe^{3+}-O_I centers in $KTaO_3$ can be aligned using linearly polarized Ar^+-ion laser light with $\lambda = 456$ nm. The alignment is observed directly via the change of the characteristic line pattern of the optically detected magnetic resonance (ODMR) of these centers. The ODMR is monitored by the magnetic circular dichroism (MCD) of absorption and is unambiguously attributed to Fe^{3+}-O_I, because the angular dependence of the ODMR lines agrees well with known electron paramagnetic resonance results. By observing the strength of the ODMR as a function of the photon energy, the MCD spectrum and, hence, the absorption bands of Fe^{3+}-O_I centers in $KTaO_3$ are identified. These bands are also found in the spectrum of the linear dichroism (LD), which is produced by photoalignment of the axial centers. The results lead to the interpretation that the orientation of Fe^{3+}-O_I has a local, molecular character and is similar to the case of F_A centers in alkali halides.

Introduction. Although cubic potassium tantalate is of lesser technical relevance than the related ferroelectrics like $KNbO_3$ or $BaTiO_3$, it is regarded as a model perovskite-type oxide.[1] It is evident that understanding the defect properties in $KTaO_3$ is of valuable help in guiding investigations of similar substances. In these oxides, iron plays an important role as an omnipresent impurity influencing the photorefractive properties. In $KTaO_3$ several defect configurations have been observed in electron paramagnetic resonance (EPR) studies for Fe^{3+},[2-4] cubic as well as axial centers, with Fe^{3+} on the K^+ or Ta^{5+} site. Some of these centers are found in EPR investigations of other oxide perovskites with very similar properties.[1] Compared to the number of EPR studies, less attention has been paid to the optical absorption of defects in $KTaO_3$ and related crystals, although this topic is apparently closely connected to electro-optic applications. Conventional optical absorption studies suffer from the fact that usually rather uncharacteristic spectra are observed and a definite attribution to the underlying impurity is difficult, as one may see, e.g., in the case of $SrTiO_3$.[5] Akishige and Ohi[6] reported on the absorption and the photochromic behavior of iron-doped $KTaO_3$ and ascribed two bands at 2.82 and 2.38 eV to Fe^{4+} and Fe^{5+}, respectively, because similar bands have been attributed to these species in $SrTiO_3$.[7] In this paper, we report on optically detected magnetic resonance (ODMR), magnetic circular dichroism (MCD), and optical alignment properties of the $Fe_K{}^{3+}$-O_I center in $KTaO_3$ first observed by Bykov *et al.*[4] This center is characterized by a surprisingly large axial crystal field parameter D=4.46 cm^{-1}. Although there are alternative interpretations of D in the framework of the superposition model,[8,9] we adopt the idea of interstitial oxygen being the defect that causes the strong axial character of this center, because both experimental work[10] and a refined theoretical analysis of D combined with shell model calculations[11] favor this model.

Experiment. The investigated crystal has been grown with K_2O surplus in oxidizing atmosphere by the top-seeded-solution-growth method at the University of Osnabrück. It was heavily doped with iron (5000 ppm Fe in the melt), added as Fe_2O_3. The sample was oriented as shown in Fig. 1 with polished (110) planes. Figure 1 also defines the light polarization angle θ and the directions of the incident light beam and the magnetic field. The low-intensity probe beam [for linear dichroism (LD), as well as for MCD] is generated by an arc lamp, passes a monochromator, linear polarizer, and photoelastic modulator, and is detected after transmission through the crystal by a S20 photomultiplier. The retardation amplitude ($\lambda/2$ for LD, $\lambda/4$ for MCD) of the modulator is automatically adjusted to follow the wavelength when spectra are recorded. An Ar^+-ion laser provides the linearly polarized light for center orientation, approximately 50 mW impinging on the sample. So far all measurements were done at 2 K (bath cryostat). As the very high dielectric constant of the sample would completely destroy the mode of a cavity, the crystal is simply positioned at the end of a waveguide leading into the cryostat. The microwave propagates along $[\bar{1}10]$ (Fig. 1). The method of ODMR detected by MCD of absorption and the tagged-MCD technique have recently been reviewed[12] and shall not be explained here.

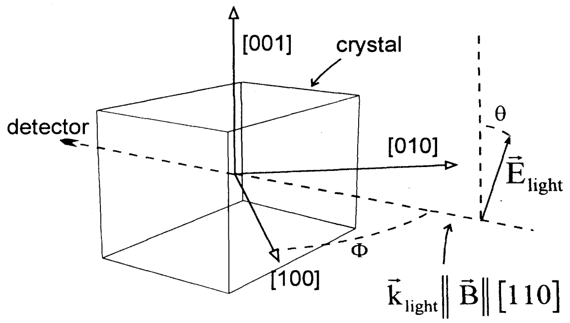

FIG. 1. Sketch of the geometry of the experimental setup. $\mathbf{k}_{light}$ stands for the propagation direction of both the probe (MCD and LD) and the laser beam (optical alignment). θ describes the direction of the polarization vector of these beams. Microwave power was shone in along $[\bar{1}10]$. The dimensions of the sample were approximately 3 × 2.5 × 2 mm^3.

Results. Without illumination by laser light, a rather well-structured MCD spectrum is seen [Fig. 2(a)]. The zero-field absorption obtained under the same conditions is shown in Fig. 2(b) for comparison. Both absorption bands at approximately 2.4 eV and 2.8 eV are at the same position as the bands found by Akishige and Ohi[6] for iron-doped $\mathrm{KTaO_3}$, but will be interpreted differently here (see Sec. IV). It is obvious that the MCD and the absorption bands are correlated. One even obtains a consistent decomposition of both spectra if it is assumed that the absorption band at 2.8 eV is split into two opposite MCD bands, shown by dash-dotted lines in Fig. 2. This feature is frequently postulated in qualitative analyses in MCD spectroscopy and the corresponding bands are called "derivativelike" or "pseudo-*A*" bands.[13] We obtained the following band positions: MCD, 2.40(5), (2.61(5), 2.90(5)), 3.4(1) eV, and absorption, 2.34(5), 2.77(5), 3.5(1) eV. The errors result mainly because of uncertainties concerning the structure of the bands close to the band edge (approximately 3.62 eV). We stress that this decomposition is not unique, but rather establishes the most plausible band structure and reveals the correlation between MCD and absorption.

Figure 3(a) shows an ODMR spectrum at 36 GHz observed by the MCD at 2.46 eV. All three lines are unambiguously identified as due to the strongly axial $\mathrm{Fe_K}^{3+}$-$\mathrm{O_I}$ center with EPR parameters $g_{xx} = g_{zz} = 2$, tetragonal symmetry with z axis $\parallel$ [100] and D=4.46 cm^{-1}.[4] The line at 420 mT ($g_{\mathrm{eff}} \approx 6$) belongs to [001] centers; the two lines at 575 mT result from the [100] and [010] centers, which are nonequivalent because of a slight misalignment ($\phi = 48.5°$; see Fig. 1). The angular dependence has been measured for $\phi = 0° - 50°$ and the result confirms the above parameters. No additional ODMR lines have been observed so far, although in conventional EPR the same crystal showed weaker signals of a second axial center with $g_{\mathrm{eff}\perp} = 4.35$ at 34 GHz (Ref. 14) and very weak signals of cubic Fe. Especially, the Fe-$\mathrm{V_O}$ center[2,4] is definitely not present in this sample, which was apparently well oxidized during growth. In contrast with the literature,[15] $\mathrm{Fe_K}^{3+}$-$\mathrm{O_I}$ is the dominant iron defect here. Figure 3(b) depicts the tagged MCD of this center. Apparently, this MCD spectrum, which is tagged to $\mathrm{Fe_K}^{3+}$-$\mathrm{O_I}$, is exactly the same as the spectrum of the total MCD, Fig. 2(a). It is commonly assumed that a tagged-MCD spectrum selectively shows the MCD of that center which undergoes ODMR transitions, and there are numerous examples which support this idea.[12] This means that the observed MCD is due to $\mathrm{Fe_K}^{3+}$-$\mathrm{O_I}$ and, consequently,

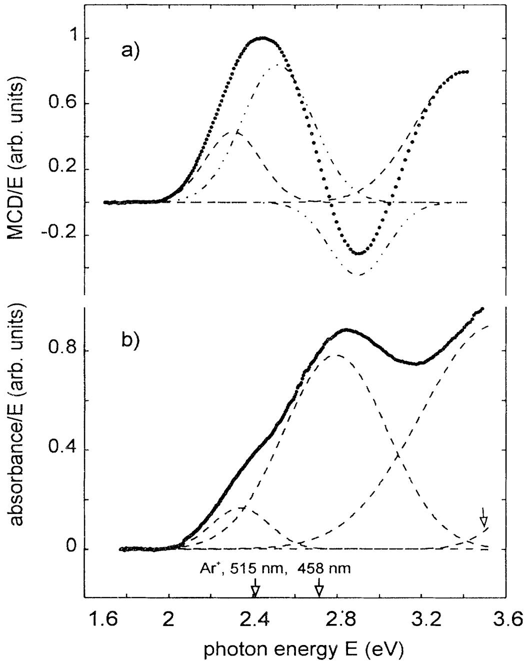

FIG. 2. (a) MCD and (b) absorbance of the $\mathrm{KTaO_3}$ crystal. Both ordinates are divided by the photon energy E to obtain the proper band shapes. The dashed lines represent fits with Gaussians, whereby the dash-dotted curves correspond to the absorption band at 2.8 eV. In part (b), the arrow points at an additional curve, which accounts for the onset of the band-band absorption in this region.

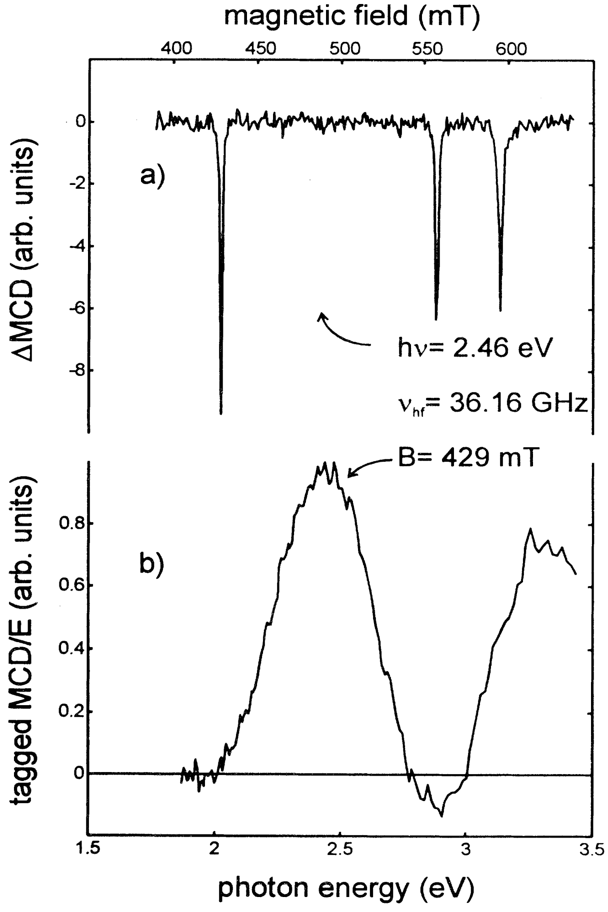

FIG. 3. (a) Change of the MCD caused by paramagnetic resonance, i.e., the ODMR signals. All three lines result from $\mathrm{Fe_K}^{3+}$-$\mathrm{O_I}$ (see text). The usually observed slope of the basis line of the MCD has been eliminated here. (b) The height of the low-field line of part (a) as a function of the photon energy E of the probe beam (divided by E, for the same reason as in Fig. 2). This type of spectrum is called a tagged-MCD spectrum.

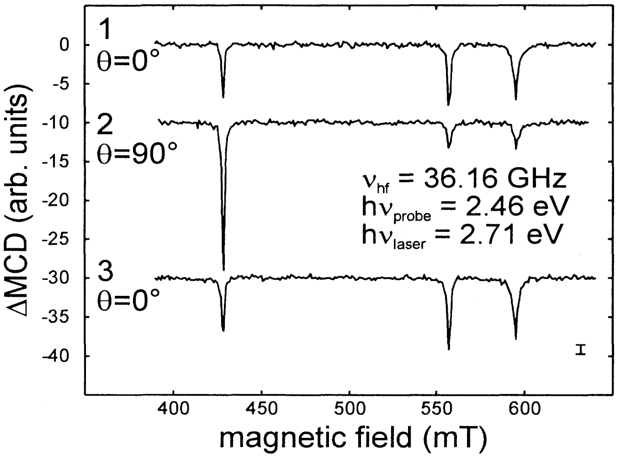

FIG. 4. ODMR spectra, as in Fig. 3(a). Trace 1, after illumination with vertically polarized laser light of 2.71 eV, $\theta = 0^{\mathrm{circ}}$ (see Fig. 1); 2, after $\theta = 90°$; and 3, again after illumination with $\theta = 0°$. Within the error given by the bar in lower right corner, the population changes of the low- and high-field centers cancel each other. The duration (approximately 5 min) and the power of the irradiation (approximately 50 mW at the sample) were sufficient to achieve an equilibrium of the population.

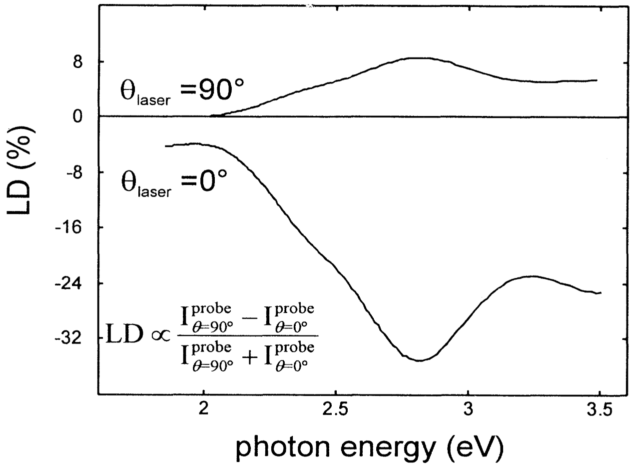

FIG. 5. The spectral dependence of the LD, as defined in the figure and calibrated in percentage. The upper curve was obtained after illumination with a horizontally polarized laser beam (see Fig. 1). This illumination corresponds to the one applied before recording the ODMR spectrum in Fig. 4, trace 2. The lower LD was measured after shining onto the sample with vertically polarized light.

that the absorption in that region [Fig. 2(b)] results predominantly from this center.

This result is further supported by optical alignment experiments: Figure 4 shows ODMR spectra like in Fig. 3(a) but after illumination with polarized laser light with $\lambda = 458$ nm. The first spectrum was measured after illumination with $\mathbf{E}_{\mathrm{laser}}$ parallel to the [001] direction (see Fig. 1), which means $\theta = 0°$, the second after irradiation with $\theta = 90°$, and the third after illuminating with $\theta = 0°$ again. The line intensities show that those $\mathrm{Fe_K}^{3+}$-$\mathrm{O_I}$ centers are depopulated whose axes are most parallel to the polarization direction. That is, for $\theta = 0°$ the number of [001] centers decreases and that of the [100] and [010] centers increases. The polarization $\theta = 90°$ yields the opposite effect, because in this case the projection of $\mathbf{E}_{\mathrm{laser}}$ on [001] is zero, while it is nonzero onto [100] and [010]. This behavior is different from the one observed for Fe^{1+}-$\mathrm{V_O}$ centers in $\mathrm{SrTiO_3}$. There, those centers are preferentially populated which are oriented *parallel* to the polarization axis.[16] Within the estimated error (see Fig. 4, bottom right), the sum of the individual line strengths is constant and the population changes are reversible. Before discussing the mechanisms causing this alignment, we present the results concerning the linear dichroism.

Figure 5 shows LD spectra which are induced by optical alignment. The LD is measured with the probe beam switching between the two orientations of polarization, $\theta = 90°$ and $\theta = 0°$. In terms of the transmitted intensities I, we define LD$= 2(I_{\theta=90} - I_{\theta=0})/(I_{\theta=90} + I_{\theta=0})$ (calibrated in percentage in Fig. 5). For other orientations, e.g., LD$' \propto (I_{\theta=45} - I_{\theta=-45})$, only very weak signals were obtained. Only positive bands are seen for $\theta_{\mathrm{laser}} = 90°$, whereas for $\theta_{\mathrm{laser}} = 0°$ only negative bands are observed. In both cases, the LD was extreme for these angles. This fact and the almost zero LD$'$ indicate that the main axes of the absorption coefficient of the underlying centers are compatible with [100] directions. The sign of the LD is such that the laser light bleaches the sample for the given polarization. The reason for the offset below 2 eV is not yet understood, as well as the strongly different amplitude. Both LD spectra were again decomposed into Gaussian bands, yielding, within scatter, the same data as for absorption. This indicates that the LD is due to $\mathrm{Fe_K}^{3+}$-$\mathrm{O_I}$ centers, as we will discuss now.

Discussion. Most of the experimental observations can be interpreted straightforwardly, assuming that $\mathrm{Fe_K}^{3+}$-$\mathrm{O_I}$ is oriented in a local ionic manner, like F_A centers in alkali halides.[17] This model agrees with the fact that during the alignment with laser light of 2.71 eV the total number of the centers remains constant. Another conceivable orientation mechanism, keeping the number of Fe-$\mathrm{O_I}$ centers constant, is the following: The Fe-$\mathrm{O_I}$ centers with axes parallel to the light polarization are ionized preferentially; the charge carriers move in the appropriate band and are trapped again at other Fe-$\mathrm{O_I}$ centers with arbitrary orientation.[18] As a consequence, charge transfer between $\mathrm{Fe_K}^{3+}$-$\mathrm{O_I}$ centers and *different* partners can be ruled out.[19] The second mechanism, the charge transfer process among Fe-$\mathrm{O_I}$ centers, could be either one of the two reactions, $\mathrm{Fe}^{2+}\text{-}\mathrm{O_I} + \mathrm{Fe}^{3+}\text{-}\mathrm{O_I} + h\nu \rightarrow \mathrm{Fe}^{3+}\text{-}\mathrm{O_I} + \mathrm{Fe}^{2+}\text{-}\mathrm{O_I}$ (electronic intervalence transfer), or the same with $\mathrm{Fe}^{4+/3+}$-$\mathrm{O_I}$ and hole transfer. The latter process may also be interpreted as an excitation of an electron from the valence band (charge transfer transition), the created hole being captured by another Fe-$\mathrm{O_I}$ center. An absorption band at 2.82 eV in $\mathrm{SrTiO_3}$ has been attributed[7] to such a charge transfer transition of cubic Fe^{4+}. As done by Akishige and Ohi,[6] one may therefore assume that the band at 2.8 eV in $KTaO_3$ has the same origin. Furthermore, this band might only be slightly influenced by the presence of the interstitial oxygen ion. Because of this and taking into account the oxidizing growth atmosphere (Fe^{2+} unlikely), we drop the first reaction as a possible explanation of the alignment process, leaving the $Fe^{4+/3+}$-related charge transfer mechanism and the purely ionic process.

In the first case, absorption starts from the charge state 4+ of iron, in the second from Fe^{3+}. This gives the key to distinguishing between the two possibilities: The fact that the MCD tagged to the resonance of $Fe_K{}^{3+}$-O_I shows the same bands as both the absorption and the LD spectra supports the local ionic orientation process. Also the results of the alignment experiments can easily be understood in this model. From Fig. 4 we see that polarized laser light produces Fe^{3+}-O_I centers with the tetragonal axis perpendicular to $\mathbf{E}_{\text{laser}}$. In a F_A center model, this means that those centers with axes parallel to $\mathbf{E}_{\text{laser}}$ must be excited more strongly than the perpendicular ones. A statistical reorientation during the subsequent deexcitation leads to an alignment along the perpendicular directions, as observed by ODMR. Preferentially parallel absorption is exactly what has to be expected from the symmetry and the electronic configuration of Fe^{3+}-O_I. The polar character of this complex therefore easily accounts for both the sign and the appreciable strength of the LD. Illumination with a green Ar-laser line (2.41 eV) did not change this population distribution. This is understood if only the excitation into the high-energy band at 3.4 eV is sufficient to overcome the barrier between the different orientations. Embedded cluster calculations will prove very useful to obtain a theoretical estimate for this barrier. Until now, one can only say that, according to the geometry of Fe^{3+}-O_I,[11] there is enough space for the entity Fe^{3+}-O_I to turn around in the oxygen cage.[20] Furthermore, the study of the thermal activation of the reorientation of the Fe^{3+}-O_I centers will yield an activation energy, which also may be compared with shell model calculations.

We conclude that the ionic orientation process is the most likely one to account for the experimental observations. This implies that $Fe_K{}^{3+}$-O_I should be regarded as a molecular complex which exhibits optical transitions, which are considerably shifted to the red in comparison with isolated Fe^{3+}. This is surely the most surprising result, since it means that the optical properties of isolated transition metal ions may be very strongly modified by associated ions, as the interstitial oxygen ion. Isolated Fe^{3+} is known to show charge transfer transitions at considerably higher energies. The coincidence of the band at 2.35 eV observed here with a band found by Akishige and Ohi[6] is accidental. These authors recorded only very weak EPR signals of axial Fe centers (either Fe-V_O or Fe-O_I, which cannot be distinguished at X-band frequencies) and attributed their band to Fe^{5+}. On the other hand, ODMR signals of Fe^{5+} should be observable at 2.35 eV if that band were due to Fe^{5+} in our crystal.

A most important result is the observation of a very strong light-induced LD. Even with unpolarized light one could orient the Fe^{3+}-O_I centers parallel to the direction of the light beam if a (100)-cut crystal were used. This would lead to a considerable increase of the transmitted light and, hence, could not be distinguished from "true" photochromism. The observed photo-LD can also be used to write holograms using orthogonally polarized waves, as has been observed recently in the garnet $Tb_3Ga_5O_{12}$.[21] Further experiments with different crystals and with chemically treated specimens are in progress.

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