P H Y S I C A L   R E V I E W   L E T T E R S

Evidence for Light-Induced Hole Polarons in LiNbO₃

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Transient light-induced absorption in LiNbO₃ is observed in the blue-green spectral range after pulsed illumination with 532 nm. Its buildup and decay in Fe-doped LiNbO₃ is satisfactorily described by a sum of two stretched exponential functions. For undoped LiNbO₃, however, only one stretched exponential decay is observed. These experimental results are explained by the formation of both small Nb_{Li}^{4+} electron polarons and O^- hole polarons. The mechanism is discussed on the basis of a proposed band scheme.

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Introduction.—Lithium niobate (LiNbO₃, LNB) is one of the most important crystalline materials for nonlinear optical applications of all kinds. It is utilized in lasers, electro-optic, acousto-optic, and optical storage devices [1]. Precise knowledge of the interaction between the electronic properties of LNB with incident light is an indispensable prerequisite for any of these applications. In this context, information about transient changes of crystal parameters such as light-induced absorption α_{li} or electric conductivity is required. One way to bring about such changes is the optical generation of polarons: When charge carriers are excited from a deep trap into a shallow trap close to the edge of the conduction band, the coulomb interaction and phonon coupling between the excited charge and the surrounding ions can lead to a local deformation of the crystal lattice, stabilizing the charge in its new position [2]. The lifetime of the polaron thus formed depends, among other things, on the temperature and the stabilization energy of the lattice deformation and ranges from a few μs to nearly infinity. The knowledge of light-induced deep or shallow traps is important for nonvolatile holographic data storage via two step recording using polarons as one step [3] and for a better understanding of unwanted absorption in the field of frequency mixing or generation, especially in periodically poled LNB.

The best-documented light-induced polaron in congruently melting iron-doped LNB, where the Li/Nb ratio is not unity but 48.4/51.6, is the small bound electron polaron generated at the most common defect, a Nb^{5+} ion on a Li^+ lattice site (Nb_{Li}), by exciting an electron from a deep Fe^{2+} trap or from the valence band by a two-photon excitation [4]. The physical properties of this polaron, such as its broad absorption band around 740 nm (1.6 eV), the EPR signals of Nb^{4+} [5–9], or the dependence of its lifetime on its distance to the nearest empty deep trap [10,11], have been described in the literature. Furthermore, the correlation of the EPR signals to the absorption band at about 1.6 eV of the Nb_{Li}^{4+} bound small polaron described in [9] is unambiguously proven by magnetic circular dichroism measurements [12]. In addition,

absorption bands around 496 nm (2.5 eV) and 400 nm (3.1 eV), induced by x or γ rays, pulsed electron or neutron beams, are reported [13–15]. They are either transient or stable, depending on how they are created. However, there has been no report on measurements of light-induced absorption changes in the blue-green spectral range, in order to determine the relaxation processes of the generated electron and hole polarons.

Therefore we present measurements of the light-induced absorption (α_{li}) in Fe-doped and undoped congruent LiNbO₃ crystals. The temporal evolution of α_{li} probed at wavelengths $458 \leq \lambda_s \leq 514$ nm is examined. The results that give strong evidence for the generation of hole polarons are explained with respect to mechanisms of population and depopulation of polaronic centers and doping levels within a presented band scheme.

Experimental details and results.—Single crystals of congruently melting LiNbO₃ (undoped and doped with 0.1 mol % Fe) were cut into plates with dimensions of $z = 10$ mm ($z \parallel c$ axis), $y = 8$ mm, and thicknesses of $x = 3$ mm (undoped) and $x = 0.52$ mm (Fe doped). The concentration of Fe^{2+} doping ions in the crystal was determined by optical absorption measurements to be $c_{Fe^{2+}} = (5.5 \pm 0.2) \times 10^{23}$ m^{-3}. A pulse of a frequency-doubled Nd-YAG laser ($\lambda_p = 532$ nm) impinged perpendicularly on the yz face of the sample. Ordinary polarization was chosen for the pump light. The pulse was characterized by a FWHM of 2.5 ns and a 10% point at 5.4 ns. The pulse energy $E_p = 150$ mJ corresponded to an intensity of $I_p = 410$ MW/cm² . The intensity $I_s(t)$ of the ordinarily polarized low-intensity probing beam of an Ar^+ laser or a diode laser at 785 nm was monitored by a Si photodiode with a rise time of less than 0.2 ns. The signal of the diode was fed to a 2 GHz storage oscilloscope. From $I_s(t)$, the light-induced absorption $\alpha_{li}(t)$ is determined by $\alpha_{li}(t) = (1/d) \ln[I_s(t=0)/I_s(t)]$, where d is the crystal thickness.

Figure 1(a) shows the temporal development of the light-induced absorption $\alpha_{li}(t)$ in undoped LNB for the probing wavelengths $\lambda_s = 458, 488, 514$, and 785 nm in the temporal range $5 \times 10^{-9} < t < 40$ s on a logarithmic
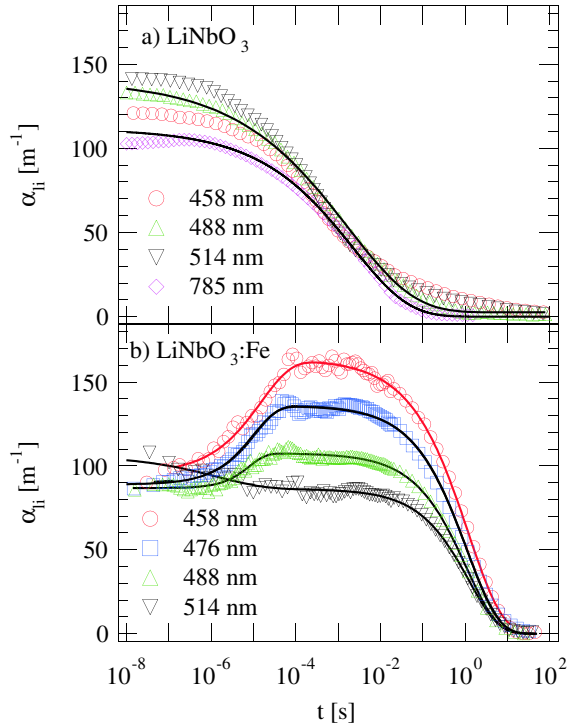
FIG. 1 (color online). Temporal development of the light-induced absorption in (a) undoped LNB and (b) LNB:Fe at various probing wavelengths λ_s ($\lambda_p = 532$ nm and $I_p = 410$ MW/cm²). The symbols represent experimental data and the lines fits to these data according to Eq. (1).

time scale. The development of $\alpha_{li}(t)$ for Fe-doped LNB is presented in Fig. 1(b) for $\lambda_s = 458, 476, 488,$ and 514 nm. For reasons of clarity the data have been thinned out and some of the probing wavelengths were omitted from the figures. Evidently the two samples show a fundamental difference in their response. In undoped LNB α_{li} continuously decreases as a function of time, independent of the probing wavelength λ_s. The initial value of α_{li} (at 10^{-8} s) increases with increasing λ_s in the blue-green spectral range, while it is lower again at 785 nm. On the other hand, in Fe-doped LNB a notable $\alpha_{li}(t)$ of about 100 m^{-1} is observed immediately after the pump pulse has subsided. For the longest probe wavelength, $\lambda_s = 514$ nm, the absorption shows a very slight decay on a time scale of 10^{-6} s and decays completely for $t > 0.01$ s. For $\lambda_s = 488$ nm, α_{li} is only about 85 m^{-1} for $t < 10^{-6}$ s, then increases to about 100 m^{-1}, peaks around $t = 10^{-4}$ s, and drops to zero within 20 s. For the shorter probing wavelengths, $\lambda_s = 458$ nm (476 nm), this behavior is even more pronounced: The curves start at $\alpha_{li} = 90$ m^{-1}, increase drastically to $\alpha_{li} = 164$ m^{-1} (136 m^{-1}) within 10^{-4} s and decay for $t > 0.01$ s. It has been shown that $\alpha_{li}(t)$ in LNB:Fe follows a stretched exponential law for probing wavelengths $\lambda_s > 590$ nm [10,11]. Correspondingly, the decay of $\alpha_{li}(t)$ in the undoped sample [Fig. 1(a)] could be fitted with one stretched exponential

function $\alpha e^{-(t/\tau)^\beta}$ for the probing wavelengths $458 < \lambda_s < 514$ nm, where α, τ, and β denote the amplitude, decay time, and stretching exponent. The buildup and decay of α_{li} in LNB:Fe [Fig. 1(b)] has to be fitted with a sum of two stretched exponential functions:

$$\alpha_{li}(t) = \alpha_1 e^{-(t/\tau_1)^{\beta_1}} + \alpha_2 e^{-(t/\tau_2)^{\beta_2}}, \quad (1)$$

where α_1, τ_1, and β_1 are the amplitude, rise time, and stretching exponent of the short-time increase and α_2, τ_2, and β_2 the corresponding parameters for the long-time decay of α_{li}. Note that α_1 is negative for wavelengths less than 500 nm but positive for larger wavelengths, while α_2 is always positive. The fit describes the data very well for the three short probing wavelengths $\lambda_s \leq 488$ nm. For $\lambda_s = 514$ and 501 nm, a fit with two stretched exponential functions and $\alpha_1, \alpha_2 > 0$ was possible albeit with difficulties; therefore the obtained values for τ_1 and β_1 have a large margin of error. The decrease of the starting amplitude is very small. The resulting fit curves are displayed as continuous lines in Fig. 1. The fit parameters are presented in Table I.

The results of the fits confirm the observations made above: The absolute value of the "rise amplitude" α_1 decreases with increasing wavelength. The same is valid for the "decay amplitude" α_2. The rise time τ_1 is constant around 10^{-5} s, and the decay time τ_2 ranges around a mean value of 1.1 s, while the stretching exponent β_2 lies around 0.6. A notable feature is the significant increase of the stretching parameter β_1 from 0.55 (458 nm) to unity

TABLE I. Parameters of the buildup (α_1, τ_1, β_1) and decay (α_2, τ_2, β_2; α, τ, β) of the light-induced absorption obtained from fits of Eq. (1) to the measured data.

λ_s (nm)	α (m^{-1})	τ (s)	β
458 (undoped)	123 ± 5	$(1.0 \pm 0.5) \times 10^{-3}$	0.25 ± 0.04
476 (undoped)	128 ± 5	$(1.2 \pm 0.5) \times 10^{-3}$	0.23 ± 0.04
488 (undoped)	134 ± 5	$(0.7 \pm 0.4) \times 10^{-3}$	0.23 ± 0.04
501 (undoped)	140 ± 5	$(1.0 \pm 0.4) \times 10^{-3}$	0.28 ± 0.04
514 (undoped)	144 ± 5	$(0.6 \pm 0.4) \times 10^{-3}$	0.26 ± 0.04
785 (undoped)	104 ± 5	$(2.5 \pm 0.4) \times 10^{-3}$	0.36 ± 0.04

λ_s (nm)	α_1 (m^{-1})	τ_1 (s)	β_1
458	-68 ± 4	$(1.0 \pm 0.5) \times 10^{-5}$	0.55 ± 0.04
476	-47 ± 3	$(1.0 \pm 0.5) \times 10^{-5}$	0.78 ± 0.04
488	-21 ± 5	$(8 \pm 2) \times 10^{-6}$	1.1 ± 0.1
501	15 ± 23	$(2 \pm 2) \times 10^{-6}$	0.2 ± 0.2
514	20 ± 4	$(1.4 \pm 0.5) \times 10^{-6}$	0.4 ± 0.1

λ_s (nm)	α_2 (m^{-1})	τ_2 (s)	β_2
458	164 ± 8	1.2 ± 0.4	0.54 ± 0.04
476	136 ± 7	1.1 ± 0.4	0.59 ± 0.04
488	108 ± 5	1.1 ± 0.4	0.60 ± 0.04
501	103 ± 5	1.1 ± 0.4	0.55 ± 0.05
514	94 ± 5	1.2 ± 0.4	0.60 ± 0.04

(488 nm) with increasing wavelength. For undoped LNB α increases with increasing wavelength, τ is much shorter than τ_2 with a mean value of 0.8×10^{-3} s, and $\beta = 0.25$ is a factor of about 2 smaller than $\beta_2 = 0.6$.

In Fig. 2 the dependence of α_{li} on the pulse intensity is presented for $\lambda_s = 488$ and 785 nm with $\lambda_p = 532$ nm. The quadratic increase of α_{li} (488 nm) demonstrates the band to band transition by two-photon absorption, generating a hole in the valence band. This nonlinear absorption is determined using shorter pulses and $\lambda_p = 388$ nm in Ref. [16]. The quadratic increase observed in our measurements is in very good agreement with these results. At $\lambda_s = 785$ nm the occupation of the empty small bound polaron state is detected [10,11]. The exponential increase is typical for the linear two state transition $Fe^{2+} \rightarrow Nb_{Li}^{4+}$ due to the depopulation of the Fe^{2+} state. Consequently, the detection of the linear or nonlinear absorption behavior depends on the used probing wavelengths. However, in both cases electrons and holes are created by irradiation with $\lambda_p = 532$ nm.

Discussion.—The buildup and decay of α_{li} in LNB:Fe for $\lambda_s < 500$ nm is different from that for longer probing wavelengths [10,11]. In the red and near-IR spectral range one observes only the excitation of electrons from Fe^{2+} centers forming small Nb_{Li}^{4+} polarons and their subsequent relaxation, whereby the conduction band acts as a short intermediate state. An explanation of the behavior of $\alpha_{li}(t)$ probed in the green and blue spectral range has to include more than just these two energetic levels. The explanation of the observed increase of $\alpha_{li}(t)$ on a time scale of a few μs is straightforward: A significant number of Fe^{2+} centers is emptied by the pump pulse. Correspondingly, the absorption band associated with Fe^{2+} around 485 nm decreases. When the Nb_{Li}^{4+}-polarons decay, the repopulation of empty Fe^{3+} centers leads to an increase of α_{li} in the blue spectral range. The best evidence for this explanation is the very good agreement between the decay time of the small
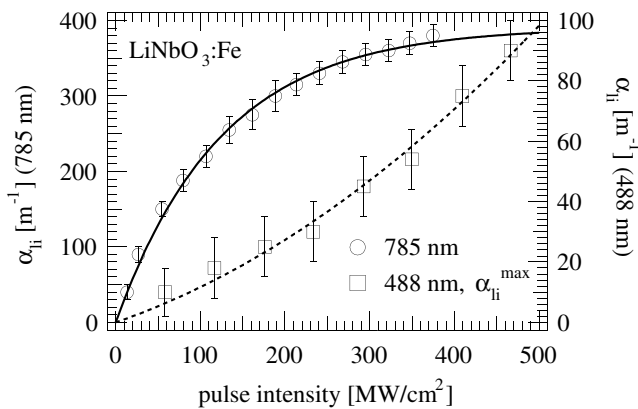

FIG. 2. Intensity dependence of the light-induced absorption for $\lambda_S = 488$ and 785 nm in Fe-doped LNB, $\lambda_p = 532$ nm. The solid line represents an exponential fit and the dashed line a quadratic fit.

bound polaron reported in the literature [10,11] and the rise time τ_1 observed here: Both are very close to 10 μs. The fact that this increase is not observed in undoped LNB is another strong evidence that it stems from the Fe doping ions. For $\lambda_s > 500$ nm, the decrease of the Fe^{2+} absorption is superposed by the simultaneous increase of the Nb_{Li}^{4+} absorption, so we do not observe an increase but rather a small decrease of $\alpha_{li}(t)$ on short time scales here. The occurrence of an isosbestic point at about 500 nm indicates that the decreasing absorption of Fe^{2+} and the increasing absorption of the Nb_{Li}^{4+} polarons cancel out each other.

The question that remains to be solved is that of the origin of the part of α_{li} with a long lifetime in the range of seconds for LNB:Fe and milliseconds for undoped LNB. No structural defects are created in the crystal by pulsed light illumination, and thus we need to be concerned only with two possibilities: The excitation of bipolarons or hole polarons. The excitation of bipolarons seems highly unlikely due to the following facts: First, a bipolaron consists of a Nb_{Li}^{4+} polaron occupying a Li lattice site and a Nb_{Nb}^{4+} polaron occupying a regular Nb lattice site, coupled by the induced lattice distortion, forming a diamagnetic system with antiparallel spins. Upon creation or decay of a bipolaron, one would thus expect to observe single Nb_{Li}^{4+} and Nb_{Nb}^{4+} polarons. Of these, only the former have been observed after pulse illumination in LNB:Fe [11]. The characteristic absorption of Nb_{Nb}^{4+} polarons around 1200 nm was not observed [9,11]. Furthermore, the nonlinear absorption of α_{li} (488 nm) in LNB:Fe and in undoped LNB demonstrates the generation of holes in the valence band by a two-photon band to band transition. They are not annihilated and can move to a pinning center. We thus conclude that the long-lived light-induced absorption in the blue-green spectral range observed here is caused by a small bound O^- polaron, i.e., a hole trapped at an oxygen ion near a lithium vacancy [4]. The decay of this polaron can be described with a stretched exponential function with a stretching exponent $\beta_2 \approx 0.6$ for LNB:Fe and $\beta \approx 0.25$ for LNB. This implies that there is no single decay time in the system, but a superposition of a multitude of decays with different decay times [10,11].

We therefore suggest the following mechanism of polaron generation by light illumination, which is depicted in Fig. 3: The pump pulse excites electrons from the deep Fe^{2+} traps by a one-photon excitation forming Nb_{Li}^{4+} polarons via the conduction band. Additionally, electrons are excited by a two-photon excitation, leaving a hole in the valence band. These electrons also form Nb_{Li}^{4+} polarons. The hole is trapped by an O^{2-} near a lithium vacancy, forming an O^- hole polaron. This excitation path is evidenced by α_{li} observed in undoped LNB. The small polarons decay within the lifetime τ_1 into the empty traps (Fe^{3+}), increasing the absorption in the blue spectral range. From there they recombine within the lifetime τ_2 with the hole polarons. As can be seen from the undoped sample,
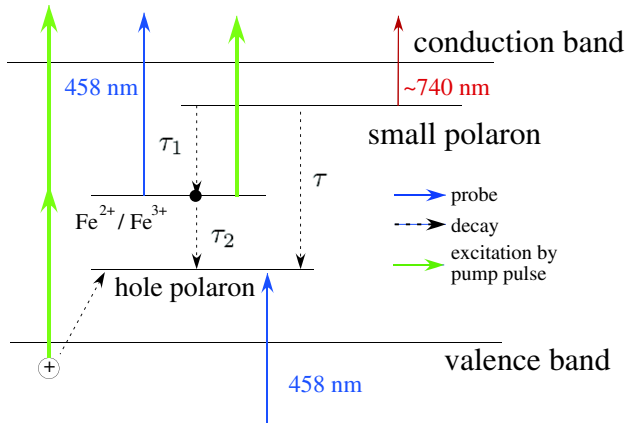
FIG. 3 (color online).   Schematic description of the different excitation and decay paths of polarons in LNB:Fe.

the recombination of the electrons from the Nb_{Li}^{4+} polarons with the holes of the O^- polarons happens in about $\tau \approx 1 \times 10^{-3}$ s probed by the absorption from the valence band into the hole polaron state. However, if empty Fe^{3+} traps are present, they will draw the electrons from the Nb_{Li}^{4+} polarons much faster within about $\tau_1 \approx 10$ μs. In these traps, the electrons are comparably stable. They recombine with the hole polarons on the longer time scale of seconds (lifetime τ_2). In the doped samples we observed no contribution to $\alpha_{li}(t)$ on a time scale of 10^{-3} s that would indicate a direct transition from Nb_{Li}^{4+} to O^-. This mechanism requires that after the pulse the number of empty Fe^{3+} traps is at least equal to the number of Nb_{Li}^{4+} polarons, which can be reached by femtosecond pulses [16]. This dependence on the Fe^{3+} concentration opens the door to a manipulation of the polaron lifetimes by changing the Fe^{2+}/Fe^{3+} ratio via a reduction/oxidation treatment or by annihilation of the hole polarons using additional irradiation with light in the blue spectral range. A further hint on the generation of O^- polarons is the intensity dependence of $\alpha_{li}(t)$, which for LNB:Fe increases exponentially into a saturation, probing at $\lambda_s = 785$ nm, but grows quadratically probing at, e.g., $\lambda_s = 488$ nm, so that the two-photon absorption is a second independent generation path of polarons besides the Fe^{2+} excitation. This means that with sufficient light intensity electrons are excited from Fe^{2+} and also from the valence band by a two-photon process via a virtual intermediate state into the conduction band. On a time scale much shorter than nanoseconds, small bound polarons are formed that relax into Fe^{3+} traps and recombine afterwards with the hole polarons. In undoped LNB the direct recombination with the hole polar-

ons occurs. Taking the cross section $\sigma = 6 \times 10^{-18}$ cm^2 measured at $\lambda_s = 776$ nm [16], one can estimate the number density of generated polarons to $n = 1.7 \times 10^{19}$ cm^{-3}, using $\alpha_{li}(785$ nm$) = 104$ cm^{-1}.

In summary, the lifetime of hole polarons in LiNbO$_3$ is reported by detecting the direct and indirect recombination processes of small bound electron polarons with hole polarons. The hole polarons are generated by a two-photon excitation from the valence band into the conduction band, whereby the hole moves to a pinning center leading to the measured absorption in the blue spectral range. The direct electron-hole recombination occurs in about 1 ms while the indirect recombination from the Fe^{3+} center needs about 1 s. The decay into the deep Fe^{3+} happens after about 10 μs. Consequently, the light-induced absorption in LiNbO$_3$ in the spectral range 400–1500 nm is generated by hole and electron polarons.

[1] L. Arizmendi, Phys. Status Solidi A **201**, 253 (2004).
[2] A. S. Alexandrov and N. F. Mott, *Polarons and Bipolarons* (World Scientific, Singapore, 1996).
[3] F. Jermann, M. Simon, and E. Krätzig, J. Opt. Soc. Am. B **12**, 2066 (1995).
[4] O. F. Schirmer and D. von der Linde, Appl. Phys. Lett. **33**, 35 (1978).
[5] L. E. Halliburton, K. L. Sweeney, and C. Y. Chen, Nucl. Instrum. Methods Phys. Res., Sect. B **1**, 344 (1984).
[6] L. Arizmendi, J. M. Cabrera, and F. Agullo-Lopez, J. Phys. C **17**, 515 (1984).
[7] O. F. Schirmer, S. Juppe, and J. Koppitz, Cryst. Lattice Defects Amorphous Mater. **16**, 353 (1987).
[8] D. A. Dutt, F. J. Feigl, and G. G. DeLeo, J. Phys. Chem. Solids **51**, 407 (1990).
[9] O. F. Schirmer, O. Thiemann, and M. Wöhlecke, J. Phys. Chem. Solids **52**, 185 (1991).
[10] D. Berben, K. Buse, S. Wevering, P. Herth, M. Imlau, and Th. Woike, J. Appl. Phys. **87**, 1034 (2000).
[11] P. Herth, D. Schaniel, Th. Woike, T. Granzow, M. Imlau, and E. Krätzig, Phys. Rev. B **71**, 125128 (2005).
[12] H. J. Reyher, R. Schulz, and O. Thiemann, Phys. Rev. B **50**, 3609 (1994).
[13] L. Grigorjeva, V. Pankratov, D. Millers, G. Corradi, and K. Polgar, Ferroelectrics **257**, 281 (2001).
[14] V. Yu. Yakovlev, E. V. Kabanova, T. Weber, and P. Paufler, Phys. Status Solidi A **185**, 423 (2001).
[15] V. Pankratov, D. Millers, L. Grigorjeva, A. O. Matkovskii, P. Potera, I. Pracka, and T. Lukasiewicz, Opt. Mater. **22**, 257 (2003).
[16] O. Beyer, D. Maxein, K. Buse, B. Sturmann, H. T. Hsieh, and D. Psaltis, Opt. Lett. **30**, 1366 (2005).