Temperature-Induced Changes of the Electronic Structure of Ferroelectric $LiTaO_3$

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A ^{181}Ta Mössbauer study of $LiTaO_3$ in the temperature range from 4.2 to 1050 K reveals temperature-induced changes of the electronic structure. Both the electric-field-gradient tensor and the total electron density at the nucleus exhibit dramatic temperature dependences. The latter reflects a charge transfer from the neighboring O ions to the central Ta ion increasing nonlinearly with temperature, an effect that has been postulated theoretically on the basis of a nonlinear anisotropic polarizability of the O ion.

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It was recently pointed out that the origin of ferroelectricity in the ABO_3 perovskites is due to a strongly anisotropic polarizability of the oxygen ion.[1] A nonlinear shell-model theory based on this assumption could in fact quantitatively explain the temperature dependence of the ferroelectric soft mode and related properties. It was further suggested that the unusual anisotropic polarizability of oxygen is due to a dynamical hybridization of the oxygen p states with d states of the transition-metal B ion.[2] With increasing temperature this should lead to a transfer of charge from the oxygen p states to d states of the transition-metal ion.

In the present Letter we show that the high-resolution 6.2-keV nuclear γ resonance of ^{181}Ta allows a quantitative study of this effect. As was realized previously,[3] the isomer shift of this nuclear γ resonance has a rather unique sensitivity to small changes of the electronic structure. Effects like the one discussed here could therefore not be detected in previous Mössbauer studies of ferroelectric systems employing mostly the ^{57}Fe γ resonance.[4]

An ideal ABO_3 system to study with ^{181}Ta Mössbauer spectroscopy is given by $LiTaO_3$, which has a ferroelectric Curie point of $T_C = 906$ K. We find that the isomer shift S increases explicitly with temperature in a nonlinear way, in agreement with the theoretically predicted O-p to Ta-d charge transfer. In addition, the main component of the electric-field-gradient (EFG) tensor at the ^{181}Ta nucleus changes drastically with temperature, which can be quantitatively accounted for on the basis of the known structural changes of $LiTaO_3$ with temperature. The observed nonvanishing asymmetry parameter η, however, cannot be explained with the known structure of $LiTaO_3$ alone.

The Mössbauer transmission experiments were performed on a 5-mg/cm^2-thick polycrystalline $LiTaO_3$ absorber, using a single-line source of ^{181}W diffused into a single crystal of tungsten. The absorber, prepared by sedimentating the finely powdered substance onto a Be disk, could be heated up to 1100 K in a resistively heated high-vacuum furnace or cooled to 4.2 K in a liquid-helium cryostat. The rest of the setup used was quite standard, employing sinusoidal source motion and an Ar-5%Kr proportional counter for γ-ray detection.

Representative spectra of $LiTaO_3$ at various temperatures are shown in Fig. 1. They are split into nineteen partly overlapping resonance lines due to electric-quadrupole splitting of the $\frac{9}{2}$-$\frac{7}{2}$ nuclear transition[5] and yield both magnitude and sign of the main component V_{zz} and the asymmetry parameter η of the EFG tensor. Figure 1 clearly shows the dramatic temperature dependence of the EFG tensor, with a change in sign of V_{zz} occurring around 800 K. The resonance spectra were least-squares fitted to a superposition of dispersion-modified Lorentzian lines,[6] yielding V_{zz}, η, and S as the main fit parameters.

The least-squares-fit results for V_{zz} and η are plotted in Fig. 2 (solid circles connected by solid lines). The open circles represent the results of a previous nuclear-quadrupole resonance study of $LiTaO_3$ at room temperature and below.[7] As is obvious from Fig. 2(a), V_{zz} varies from about 3×10^{17} to about -2×10^{17} V/cm^2 when the temperature is raised from 4.2 K to $\simeq$1000 K, with a sign change occurring around 800 K (indicated by a horizontal arrow).

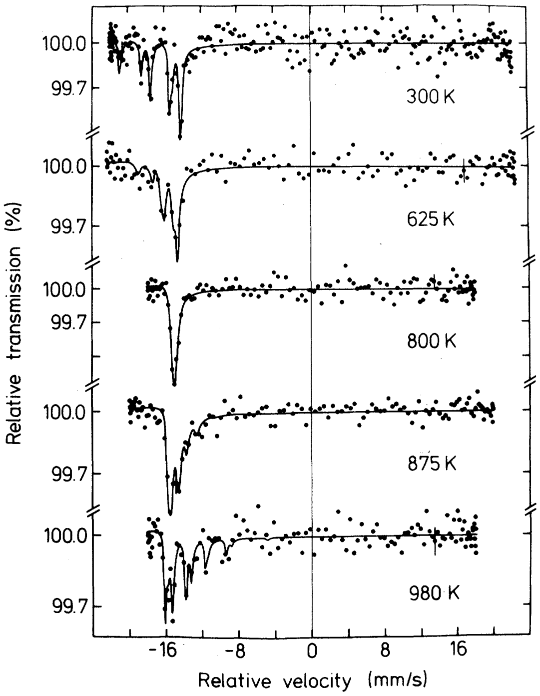

FIG. 1. ^{181}Ta Mössbauer transmission spectra of $LiTaO_3$ as a function of temperature. The solid lines represent the results of the least-squares analysis.

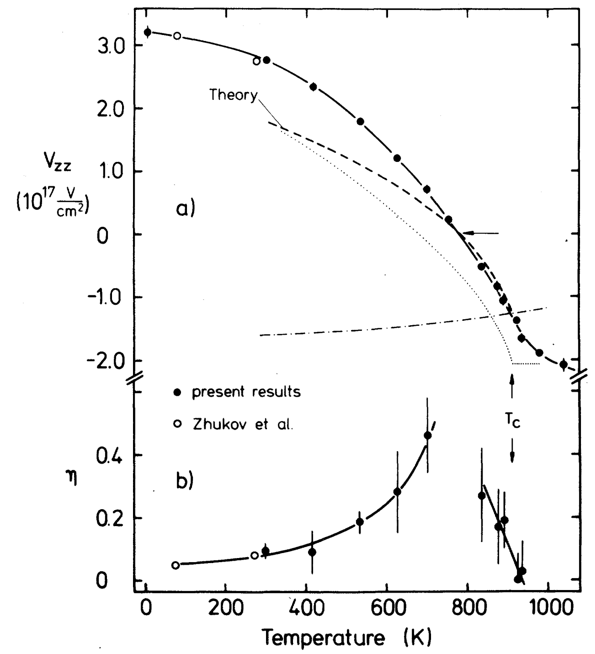

FIG. 2. Temperature dependence of the electric-field-gradient tensor at the Ta site in $LiTaO_3$: (a) main component V_{zz}, (b) asymmetry parameter η. Solid lines, experiment; dashed line, result of point-charge calculation for V_{zz}. Dash-dotted line, theoretical result without ferroelectric displacement; dotted line, theoretical result with ferroelectric displacement but constant volume.

In order to clarify the origin of the relative variation of V_{zz} with temperature, point-charge EFG calculations were performed with the method of de Wette[8] and with use of the well-known interatomic displacements in ferroelectric $LiTaO_3$ as a function of temperature.[9] The dashed line in Fig. 2(a) represents the results of this calculation, employing a lattice Sternheimer factor of $(1-\gamma_\infty)=60$ and effective charges as in Ref. 10. The agreement with the experimental data is very satisfactory, especially with the sign change being reproduced at the right temperature. In order to discuss the effect of the ferroelectric displacement of the Ta ion, $z_{\mathrm{Ta}}(T)$, on the EFG tensor, the results of two further calculations are included in Fig. 2(a). The dash-dotted curve was obtained under the assumption that $z_{\mathrm{Ta}}(T)=0$ and with use of the actual lattice expansion with temperature. The dotted curve, on the other hand, represents the results of a calculation with the actual $z_{\mathrm{Ta}}(T)$, but assuming that the unit cell does not change with temperature. These model calculations show that there are two main contributions to the EFG in $LiTaO_3$: a weakly temperature-dependent negative one due to the hexagonal lattice, and a strongly temperature-dependent positive contribution due to the ferroelectric displacement $z_{\mathrm{Ta}}(T)$. Above T_C the second contribution is expected to vanish. The experimental results above T_C, however, indicate dynamical contributions to V_{zz} as caused, e.g., by structural fluctuations of the Li ions.[9] This latter aspect can be clarified further when more data above T_C become available.

It is obvious from Fig. 2(b) that the asymmetry parameter η is unequal to 0 in the whole ferroelectric region, where the increase of η around 800 K is caused by the zero crossing of V_{zz} and not connected with T_C. Our room-temperature result for η ($\eta=0.09\pm0.03$) is in good agreement with that of Ref. 7 ($\eta=0.08$). Neutron and x-ray diffraction measurements,[9] however, have shown that the structure of $LiTaO_3$ can be described by the space group $R\bar{3}c$ (or $R3c$) in the paraelectric (or ferroelectric) region. An axially symmetric EFG tensor with $\eta=0$ is therefore expected in both regions. It is presently not clear whether static or dynamic effects are causing the observed nonaxiality of the EFG tensor, since a rather small distortion of the O octahedron in the ferroelectric phase would be sufficient. On the other hand, dynamic contributions due to anisotropic thermal vibrations of the O neighbors[9] could also account for the observed effect.

The temperature dependence of the line shift S of the resonance spectrum (relative to a W source) is plotted in Fig. 3 (solid points and solid curve). We may write $S = S_{\mathrm{SOD}} + S_{\mathrm{IS}}$, where S_{SOD} represents the second-order Doppler shift and S_{IS} the isomer shift [due to differences in the total electron density $\rho(0)$ at the ^{181}Ta nucleus]. Above room temperature, the temperature dependence of S_{SOD} is approximately given by $(\partial S_{\mathrm{SOD}}/\partial T)_P \simeq -2.3\times10^{-4}$ mm/s • deg (Ref. 3) (indicated by the dotted line in Fig. 3), while the slopes $(\partial S/\partial T)_P$ of the experimental curve are $+(32\pm5)\times10^{-4}$ mm/s • deg at 300 K and $+(62\pm5)\times10^{-4}$ mm/s • deg at 1000 K, respectively. Accordingly, the observed temperature-induced line shifts are 14 to 27 times larger and of opposite sign than the second-order Doppler shift. Therefore, the dominant contribution to $\partial S/\partial T$ stems from a strongly nonlinear variation of $\rho(0)$ with temperature. Since the change of the mean-squared nuclear charge radius is negative for the 6.2-keV γ transition of ^{181}Ta,[11] the observed increase of the isomer shift with temperature corresponds to a decrease of $\rho(0)$.

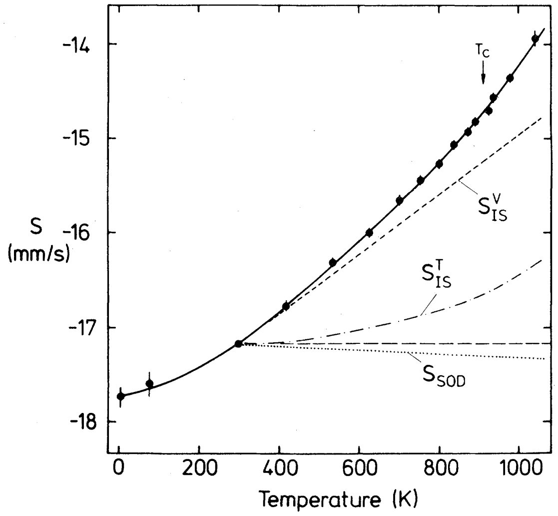

FIG. 3. Variation of the line shift S of the ^{181}Ta resonance spectrum with temperature. The line shift as a function of temperature (relative to 300 K) is decomposed in three main contributions. Dotted line, thermal redshift S_{SOD}; short-dashed line, volume-dependent part $S_{\mathrm{IS}}{}^{V}$; dash-dotted line, explicitly temperature-dependent contribution $S_{\mathrm{IS}}{}^{T}$. The long-dashed line represents the line shift at 300 K and serves as a guideline to the eye.

There are two contributions to the temperature-induced change of the isomer shift

$$S_{\mathrm{IS}}(T) = S_{\mathrm{IS}}{}^{V}(T) + S_{\mathrm{IS}}{}^{T}(T). \qquad (1)$$

The first term in Eq. (1) represents the implicit variation due to volume expansion

$$(\partial S_{\mathrm{IS}}{}^{V}/\partial T)_P = (\partial S_{\mathrm{IS}}/\partial \ln V)_T(\partial \ln V/\partial T)_P, \qquad (2)$$

while the second term describes an explicit temperature dependence at constant volume caused by a change of the local electronic structure of the Ta ion with temperature. A quantitative separation of $S_{\mathrm{IS}}(T)$ into the two contributions of Eq. (1) requires a knowledge of the volume dependence of the isomer shift, $(\partial S_{\mathrm{IS}}/\partial \ln V)_T$, which can be obtained from high-pressure experiments. Since such data are presently not available for $\mathrm{LiTaO_3}$ we estimate $(\partial S_{\mathrm{IS}}/\partial \ln V)_T \simeq 100$ mm/s • deg for $\mathrm{LiTaO_3}$ from the result for Ta metal (135 mm/s • deg)[12] and from systematics of $(\partial S_{\mathrm{IS}}/\partial \ln V)_T$ values for other metallic and nonmetallic compounds of transition elements.[13] Using this value and the known temperature dependence of the unit-cell volume of $\mathrm{LiTaO_3}$,[9] the dashed curve in Fig. 3 is obtained for $S_{\mathrm{IS}}{}^{V}(T)$. The explicit temperature dependence of the isomer shift, $S_{\mathrm{IS}}{}^{T}(T)$, which is equal to the difference between the experimental points and the sum of $S_{\mathrm{SOD}}(T) + S_{\mathrm{IS}}{}^{V}(T)$, is given by the dash-dotted curve in Fig. 3. It corresponds to a strongly nonlinear decrease of $\rho(0)$ explicitly with temperature, as caused, e.g., by a transfer of charge from O-p states to d states of the central Ta ion. An increase in the population of Ta-5d orbitals will cause a decrease of $\rho(0)$ due to an increased screening effect.[11] This is exactly the mechanism postulated by the theory of Bilz and co-workers.[1,2] For a more quantitative comparison with the theoretical predictions, high-pressure experiments on $\mathrm{LiTaO_3}$ are in progress.

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Band-Gap-Resonant Nonlinear Refraction in III-V Semiconductors

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We present experimental measurements of the resonance of the large intensity dependence of refractive index in InSb near the band-gap energy at 77 K and derive a semiempirical theory for this effect which fits the measurements well, both in absolute magnitude and wavelength dependence, using only measurable parameters. The size of the effect in other nondegenerate direct–band-gap III-V compound semiconductors and at other temperatures is predicted.

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Direct–narrow-gap semiconductors present unique situations which give large optical saturation effects in solids at low powers, particularly in the region near the band-gap energy where the effective optical matrix element for direct transitions is large and the density-of-states changes rapidly whence such saturation leads both to nonlinear absorption and to a strong intensity dependence of refractive index. We have observed this nonlinear refraction at 77 K in the semiconductor InSb obtaining $dn/dI \equiv n_2$ as high as 1 cm^2/kW [equivalent to an effective degenerate $\chi^{(3)}(\omega;\omega,-\omega,\omega)$ of ~ 1.0 esu]. This effect has already proved to be the important mechanism in the observation of optical bistability,[1,2] optical transistor action,[2,3] and degenerate four-wave mixing[4] thus demonstrating nonlinear optical devices operating at milliwatt powers.

In this paper, we present the first measurements of the resonance of nonlinear refraction (n_2) in the semiconductor InSb near its optical band gap at 77 K under which conditions nondegenerate (Boltzmann) statistics prevail. A semiempirical model is derived which uses only measurable parameters and predicts the size and sign of nonlinear refraction due to saturation and the frequency dependence of its resonance for nondegenerate direct–band-gap III-V compound semiconductors in general when excitonic effects are negligible; this is compared with the experimental results.

Existing models which have been proposed for band-gap–resonant nonlinear refraction have either adopted a full–density-matrix approach[5,6] leading to adjustable parameters (e.g., T_2) which are difficult to explain and measure, or have been restricted to low temperatures (dynamic Burstein-Moss shift)[5,7]; in no case has it been possible to explain the detailed resonance of n_2. The present theory is one extreme limit of the density-matrix approach, with intraband relaxation being sufficiently strong to thermalize the carrier distribution in times much less than the recombination time. For these thermal distributions, the simple Kramers-Krönig relations, not generally valid for nonlinear optical processes,[8] are again applicable because the quantum-mechanical phases of the carriers have been randomized by the thermalizing collisions. The theory rests on the following mechanism:

(i) A fraction of optical absorption in the semiconductor at the photon energy of interest (which may be below the band gap) results in the creation of free electrons and holes in the semicon-