Refractive indices of lithium niobate as a function of wavelength and composition

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An interferometric method is applied to determine the refractive indices of lithium niobate single crystals over a wide wavelength and composition range. A generalized two term Sellmeier equation is proposed that describes the refractive indices as a function of wavelength and stoichiometry. On the basis of this generalized Sellmeier equation the parameters of nearly all optical characterization methods for $LiNbO_3$ can be calculated. By means of a Kramers–Kronig analysis the shift in the UV absorption edge and the change in the extraordinary refractive index with the composition can be referred to each other. Excellent agreement is found with the respective experimental values.

I. INTRODUCTION

In the last decades lithium niobate has become one of the most important ferroelectric materials. Its interesting acoustical, piezoelectrical, electro-optical, nonlinear optical, and photorefractive properties have been intensively studied.[1–3] Lithium niobate can be grown with Li deficits up to 4% with respect to the stoichiometric composition, providing a comparably wide composition range for $LiNbO_3$ single crystals. Since several of the crystal properties are sensitively influenced by the Li content, precise information on the stoichiometry is desirable.

Several methods for the determination of the crystal composition have been developed. They all make use of strongly composition-dependent properties like the Curie temperature,[2] the optical absorption edge,[4] or the birefringence[5] at a fixed wavelength. Nonlinear optical techniques like the measurement of the phase matching temperature[6] or the phase matching angle for second harmonic generation utilize the birefringence between different wavelengths. Newly presented methods use anisotropic diffraction by photorefractive gratings[7] and noncolinear frequency doubling.[8]

As nearly all of these properties depend directly or indirectly on the refractive indices, measurements of the absolute indices of refraction are of great interest. Here we present interferometric measurements of the refractive indices of $LiNbO_3$ with compositions in the range of 46.1–50.0 mol % Li_2O over a wavelength range from 405 to 1176 nm. A generalized Sellmeier equation is derived that describes the measured refractive indices. The measured refractive index data and absorption data will be compared by means of a Kramers–Kronig analysis.

II. EXPERIMENT

The method of interferometric determination of refractive indices uses a Michelson-type interferometer with a rotating parallel-plate sample in one arm. The rotation axis and the *c* axis of the crystal are parallel to each other and perpendicular to the direction of the incident beam. By polarizing the light parallel or perpendicular to the rotation axis it is possible to measure the extraordinary and the ordinary refractive index, respectively.[9]

Because the interference order changes by a large amount when the crystal is inserted in one arm of the interferometer, it is impossible to measure the total change in the optical pathlength directly. Therefore, the method determines the shift in the optical pathlength when a crystal is rotated away from normal incidence by detecting the change of the interference fringes. The resulting interferogram—the light intensity at the interferometer output as a function of the rotation angle—is measured by a computer controlled setup. An accuracy of about 5×10^{-4} in the absolute refractive index is achieved by including numerical fit procedures in the evaluation.[10] Deviations from the ideal plane parallel geometry of the sample (slight wedge or lens shape) have only moderate effects on the accuracy.

A helium-neon laser served as a light source in the visible and near infrared region. A mercury vapor lamp combined with a 0.2 m monochromator was used for measurement in the short wavelength region.

Six well-characterized samples[11,12] with Li contents varying from 46.1 to 50.0 mol % Li_2O were included in our measurements. The error in the determination of the compositions can be assumed to be less than 0.2 mol % Li_2O. The homogeneity of the crystals was checked by spatially resolved second harmonic generation[13,14] and found to be much better than the composition uncertainty. The typical size after cutting and polishing was about $8\times8\times8$ mm^3, which is well suited for precise refractive index measurements.

III. RESULTS AND DISCUSSION

A. Generalized Sellmeier equation

Since $LiNbO_3$ crystals can be grown with comparably strongly varying compositions it is desirable to develop a description of the refractive indices not only valid for one fixed composition but for the whole composition range. A physical reasonable approach is to apply the dependence of the defect structure on the composition of $LiNbO_3$ as pro-

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posed by Abrahams and Marsh.[15] According to their model, in Li-deficient $LiNbO_3$ each missing Li^+ ion is replaced by an Nb^{5+} ion with compensating vacancies at the Nb site maintaining charge neutrality. In a formula representation this reads $[Li_{1-\delta}Nb_\delta]Nb_{1-4\delta/5}O_3$ with δ denoting the ratio of Li sites occupied by Nb^{5+} ions. In stoichiometric $LiNbO_3$ no atomic disorder was detected, so in a simple approximation the corresponding refractive indices may be calculated from a one term Sellmeier equation $n^2 = 1+\tilde{A}_0/(1-\lambda_0^2/\lambda^2)$ with an average oscillator position λ_0 and a parameter $\tilde{A}_0$, which is a measure of the average oscillator strength.

A deviation from the stoichiometric composition towards the direction of the Li deficiency leads to an increase in the amount of Nb^{5+} ions on Li sites, which may be described by a second oscillator term $\tilde{A}_1/(1-\lambda_1^2/\lambda^2)$ in the Sellmeier equation. Since the oscillator strength is proportional to the number of oscillators per volume, one can assume the oscillator strength $\tilde{A}_1$ of the second term to depend linearly on the amount of Nb on Li sites, whereas λ_1 remains unchanged.

The composition dependence of the first oscillator term is more complicated because of its parameters being averaged values of several oscillators. The main contribution to the refractive index is supposed to come from the NbO_6 octahedron[16] determining the lower boundary of the conduction band (d orbitals of Nb^{5+} cations) and the upper boundary of the valence band (p orbitals of O^{2-} anions). The corresponding oscillators are transitions from the valence band into the conduction band (depending on the amount of Nb on the Nb site) and excitations of plasma vibrations in the filled valence band (depending on the number of oxygen ions). These effects can be described by

$$n^2 = 1+\frac{\tilde{A}_0(\delta)}{1-\lambda_0^2/\lambda^2}+\frac{\tilde{A}_1(\delta)}{1-\lambda_1^2/\lambda^2}, \qquad (1)$$

with

$$\tilde{A}_0(\delta) = \tilde{A}_0(1-\gamma\delta) \qquad (2)$$

and

$$\tilde{A}_1(\delta) = \tilde{A}_1\delta, \qquad (3)$$

where γ has a value between $\gamma=0$ (only contributions from plasmons, dependent on O^{2-} content) and $\gamma=\frac{4}{5}$ (only transitions into the conduction band, dependent on Nb^{5+} content). Since the correct value of this parameter is unknown, several fits with varying values of γ were carried out but no significant improvements in the standard deviation were achieved. So, for reasons of convenience and simplicity, we chose $\gamma = 3/10$, which together with the relation

$$\delta = \frac{10}{3}\,\frac{50-c_{Li}}{100} \qquad (4)$$

reduces Eqs. (1), (2), and (3) to

$$n_i^2 = 1+\frac{50+c_{Li}}{100}\,\frac{A_{0,i}}{1-\lambda_{0,i}^2/\lambda^2}+\frac{50-c_{Li}}{100}\,\frac{A_{1,i}}{1-\lambda_{1,i}^2/\lambda^2}, \qquad (5)$$

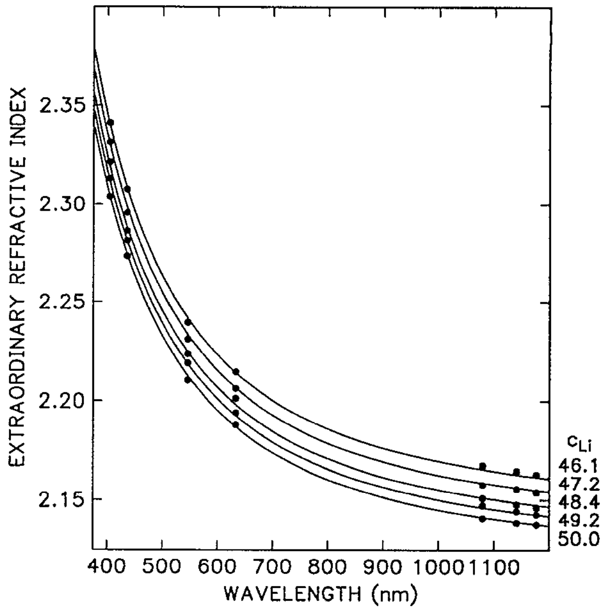

FIG. 1. Extraordinary refractive indices of $LiNbO_3$ as a function of wavelength for various crystal compositions. The curves are calculated from the generalized Sellmeier equation discussed here.

with c_{Li} denoting the Li content in mol % Li_2O. If we fit this generalized Sellmeier equation to the experimental data, we obtain a set of four coefficients ($A_{0,i}, \lambda_{0,i}, A_{1,i}, \lambda_{1,i}$) each for the ordinary ($i=o$) and the extraordinary ($i=e$) index of refraction.

The measured data for the extraordinary refractive index and the respective Sellmeier fits are plotted in Fig. 1. The agreement between experimental data and the numerical fits is excellent. The standard deviation is 1.8×10^{-3}, which is mainly due to uncertainties in the concentration data. Similar agreement is found for the ordinary refractive index. The numerical results are given in Table I.

With expression (5) it is now possible to calculate the parameters of several methods that have been proposed for the determination of the crystal composition of $LiNbO_3$.

1. Birefringence

In Fig. 2 the birefringence at 633 nm is shown. In the concentration range considered the calculated curve has a linear shape, which agrees well with our birefringence measurements. The results of Hofmann,[17] Carruthers *et al.*,[2] and Jundt *et al.*[18] are in good agreement also. Moreover, it

TABLE I. Parameters of the two term Sellmeier equation.

$$n_i^2 = 1+\frac{50+c_{Li}}{100}\,\frac{A_{0,i}}{1-\lambda_{0,i}^2/\lambda^2}+\frac{50-c_{Li}}{100}\,\frac{A_{1,i}}{1-\lambda_{1,i}^2/\lambda^2}$$

c_{Li} = mol % Li_2O; λ in nm; $i=e,o$

n_o	n_e
$A_{0,o}=3.854$	$A_{0,e}=3.489$
$\lambda_{0,o}=186.535$ nm	$\lambda_{0,e}=176.466$ nm
$A_{1,o}=3.552$	$A_{1,e}=6.004$
$\lambda_{1,o}=208.592$ nm	$\lambda_{1,e}=223.479$ nm

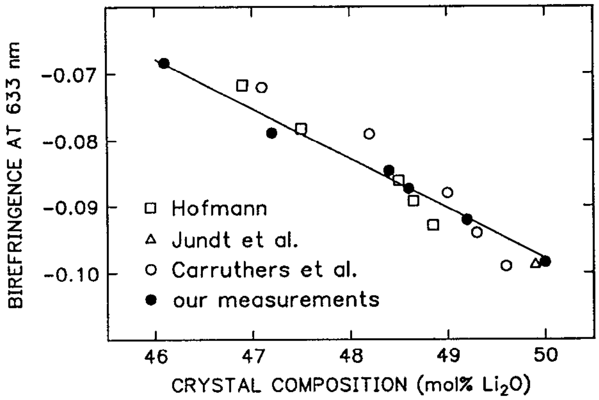

FIG. 2. Birefringence of $LiNbO_3$ at 633 nm vs crystal composition. The curve is computed from a two term Sellmeier equation.

is possible to derive a general relation between the composition and the birefringence at an arbitrary wavelength. Using

$$\alpha_i = 1 + \frac{A_{0,i}}{1-\lambda_{0,i}^2/\lambda^2},$$

$$\beta_i = \frac{A_{1,i}}{1-\lambda_{1,i}^2/\lambda^2} - \frac{A_{0,i}}{1-\lambda_{0,i}^2/\lambda^2}, \qquad (6)$$

Eq. (5) can be written as

$$n_i = \sqrt{\alpha_i + \frac{50-c_{\mathrm{Li}}}{100}\beta_i} \approx \sqrt{\alpha_i} + \frac{50-c_{\mathrm{Li}}}{100}\frac{\beta_i}{2\sqrt{\alpha_i}}, \qquad (7)$$

which yields for the birefringence $\Delta n = n_e - n_o$

$$\Delta n(\lambda) = [c_{\mathrm{Li}} - a(\lambda)]/b(\lambda), \qquad (8)$$

with

$$b(\lambda) = -100\left(\frac{\beta_e}{2\sqrt{\alpha_e}} - \frac{\beta_o}{2\sqrt{\alpha_o}}\right)^{-1},$$

$$a(\lambda) = 50 - (\sqrt{\alpha_e} - \sqrt{\alpha_o})b(\lambda). \qquad (9)$$

So for any wavelength in the investigated region it is possible to state a calibration curve for the determination of the Li content using birefringence measurements.[12]

2. Anisotropic holographic diffraction

This method (here referred to as AHD) uses the photorefractive effect to create a diffraction grating inside the crystal.[7] Two intense extraordinary polarized laser beams are crossed under an angle of 2θ to form this grating. When reading out the grating by an extraordinary beam at an angle φ^{AHD} different from θ, an *ordinary* beam is diffracted when the condition for the momentum conservation can be satisfied. This happens when φ^{AHD} obeys the equation

$$(\sin\varphi^{\mathrm{AHD}} + \sin\theta)4\sin\theta = n_o^2 - n_e^2. \qquad (10)$$

As $n_o^2 - n_e^2$ is composition dependent, the method can be used to measure the Li content in $LiNbO_3$. To compare our numerical results with experimental values, we calculated φ^{AHD} as a function of the crystal composition for the experimental conditions Arizmendi had used. The melt compositions given by Arizmendi[7] were transposed to crystal compositions.[11,12] The comparison between experimental and calculated values—shown in Fig. 3—reveals excellent agreement.

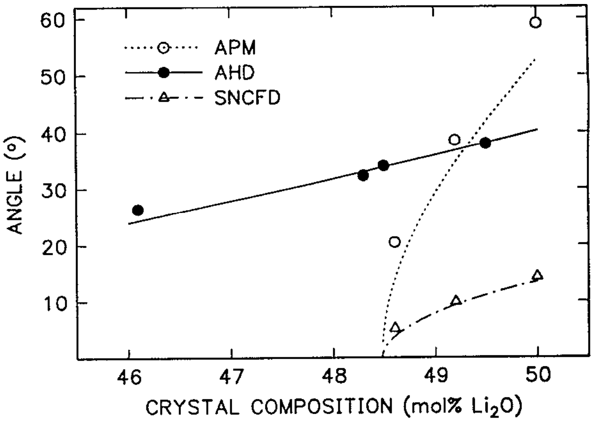

FIG. 3. Results of anistropic holographic diffraction (AHD, experimental data according to Arizmendi), spontaneous noncolinear frequency doubling (SNCFD), and angle phase matching (APM) as a function of the crystal composition of $LiNbO_3$. The angles are measured outside the crystal. The curves are derived from the generalized Sellmeier equation.

3. Spontaneous noncolinear frequency doubling

This newly presented method (SNCFD[8]) uses an intense laser beam $\mathbf{k}(\lambda_1)$, which, together with the Rayleigh scattered light $\mathbf{k}'(\lambda_1)$, obeys the vectorial phase matching condition $\mathbf{k}(\lambda_1) + \mathbf{k}'(\lambda_1) = \mathbf{k}(\lambda_2)$. The angle $\varphi_{\mathrm{cryst}}^{\mathrm{SNCFD}}$ inside the crystal of the resulting cone of second harmonic light is defined by the expression

$$\cos\varphi_{\mathrm{cryst}}^{\mathrm{SNCFD}} = \frac{n_e(\lambda_2)}{n_o(\lambda_1)}, \qquad (11)$$

which can be referred to as the angle outside the crystal $\varphi_{\mathrm{air}}^{\mathrm{SNCFD}}$ by the Snellius law. The composition dependence of this SNCFD angle for a fundamental wavelength of $\lambda_1 = 1064$ nm is shown in Fig. 3. Our experimental data (triangles in Fig. 3) agree with this calculation. The curve shows a lower concentration limit for the application of this technique of 48.48 mol % Li_2O. Since the cone angle at this point converges to $\varphi_{\mathrm{air}}^{\mathrm{SNCFD}} = 0°$ (colinear), second harmonic generation at room temperature will be observed. A recently proposed equation for the Li concentration as a function of phase matching temperature[6] reveals 48.51 mol % for $T_{\mathrm{PM}} = 20\,°\mathrm{C}$.

4. Phase matching angle

The phase matching angles of type I angle phase matching (APM) can be calculated by reducing the condition $k_o(\lambda_1) = k_e(\lambda_2)$ for the k vectors to $n_o(\lambda_1) = n_{\mathrm{eff}}(\lambda_2, \varphi_{\mathrm{cryst}}^{\mathrm{APM}})$, where $\varphi_{\mathrm{cryst}}^{\mathrm{APM}}$ is the angle inside the crystal. Applying the Snellius law one obtains for the phase matching angle $\varphi_{\mathrm{air}}^{\mathrm{APM}}$ outside the crystal

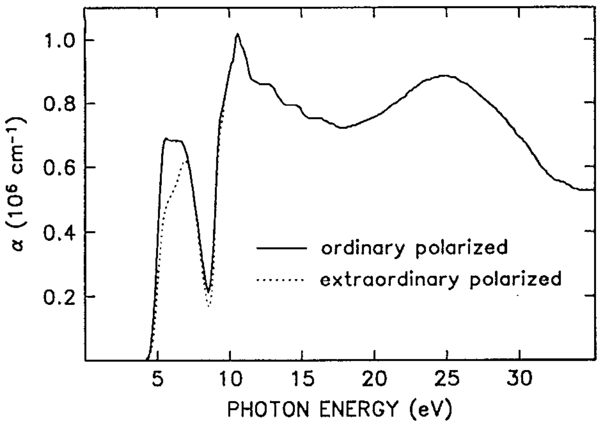

FIG. 4. Absorption coefficient α of $LiNbO_3$ as a function of energy (according to Refs. 19–21, 16).

$$\sin \varphi_{\mathrm{air}}^{\mathrm{APM}} = n_o(\lambda_1)\sqrt{\frac{n_o(\lambda_1)+n_e(\lambda_2)}{n_o(\lambda_2)+n_e(\lambda_2)}\,\frac{n_o(\lambda_1)-n_e(\lambda_2)}{n_o(\lambda_2)-n_e(\lambda_2)}}. \tag{12}$$

Calculated and experimental values for $\lambda_1 = 1064$ nm are shown in Fig. 3. The deviation of the experimental data from the calculated curve of about 10% is due to the fact that sin φ mainly depends on the difference between refractive indices. In contrast to the calculation of $n_o(\lambda_2) - n_e(\lambda_2)$, which yields a rather high accuracy, the evaluation of $n_o(\lambda_1) - n_e(\lambda_2)$ involves a systematic error. This is caused by the rather simple form of the generalized Sellmeier equation with only two oscillators in the UV region. Adding a third term (see, for example, Ref. 18) to describe the contribution from oscillators in the IR would improve the accuracy of the refractive index dispersion and accordingly of the phase matching angles, but would reduce the simplicity of the model.

B. Kramers–Kronig analysis

Since the Sellmeier equations are based on a simple model, a detailed interpretation of the fitted parameters is difficult. If we consider an oscillator term to be associated with an absorption maximum, a comparison with absorption data should be carried out.

These data can be obtained for congruent lithium niobate crystals from Földváry *et al.*[19] and Redfield and Burke[20] for the lower energy range. In the range from 5 to 35 eV data exist that are based on reflection measurements by Mamedov.[16] Only Wiesendanger and Güntherodt observed a considerable difference between the reflection of ordinary and extraordinary polarized light.[21] With slight corrections for continuity the absorption coefficients are now available for ordinary and extraordinary polarized light over a wide energy range (Fig. 4).

The determined oscillator positions of the first oscillator term in the Sellmeier equation (5) are 186.5 nm (6.65 eV) and 176.5 nm (7.03 eV) for ordinary and extraordinary polarized light. This corresponds with the broad peak in the absorption spectrum in the range from 5 to 7 eV. The asymmetric shape of the absorption curve in this region for extraordinary polarization shifts the average oscillator position to higher energies. Additionally the absorption is lower, which because of the lower oscillator strength causes the parameter A_0 to be lower (3.49 vs 3.85). Thus, the birefringence of lithium niobate seems to be mainly due to the difference of the absorption spectra in this region.

The second term of the generalized Sellmeier equation, however, cannot be evaluated in this way due to the lack of composition-dependent absorption data in the respective region. Only the lower energy range of the absorption edge was studied as a function of Li content by Földváry *et al.*,[19] Redfield and Burke,[20] and Schmidt.[22]

The observed shift in the absorption edge can be referred to the shift in the refractive index by means of a Kramers–Kronig analysis. The real part n of the complex refractive index $\tilde{n} = n + ik$ is expressed as a function of the absorption constant k by

$$n = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' k(\omega')}{\omega'^2 - \omega^2}\, d\omega', \tag{13}$$

where P denotes the principal value of the integral expression.[23] The absorption coefficient $\alpha(\omega) = k(\omega) 2\omega/c$ is commonly measured as a function of the energy $E = \omega\hbar/e$ (in eV). Thus Eq. (13) transforms to

$$n = 1 + \frac{c\hbar}{e\pi} P \int_0^\infty \frac{\alpha(E')}{E'^2 - E^2}\, dE'. \tag{14}$$

In order to refer the compositional shift in the absorption spectrum to the respective refractive index change we differentiate Eq. (14) with respect to composition x and get

$$\frac{\partial n}{\partial x} = \frac{c\hbar}{e\pi} P \int_0^\infty \frac{\partial \alpha(E')}{\partial x} \bigg/ (E'^2 - E^2)\, dE'. \tag{15}$$

For the further calculation we assume that not only the absorption edge is shifted but the whole spectrum. This is a reasonable approximation as the high energetic part of the absorption curve affects the refractive index only with a factor $1/(E'^2 - E^2)$. The differential quotient in the integrand can be written as

$$\frac{\partial \alpha(E')}{\partial x} = \frac{\partial \alpha(E')}{\partial E'} \frac{\partial E'}{\partial x}, \tag{16}$$

where $\partial E'/\partial x$ denotes the energetic shift of the absorption spectrum. Under the above assumption this shift is energy independent and so also describes the shift in the absorption edge $\partial E_A/\partial x$. It can be drawn out of the integral; thus, the shift in the absorption edge and the refractive index change refer to each other by

$$\frac{\partial n}{\partial x} = \frac{\partial E_A}{\partial x} \frac{c\hbar}{e\pi} P \int_0^\infty \frac{\partial \alpha(E')}{\partial E'} \bigg/ (E'^2 - E^2)\, dE'. \tag{17}$$

The integral can be calculated by first doing a partial integration to eliminate the differential term and then computing the result numerically using the experimental absorption data. Although there are no absorption data available for energies higher than 35 eV the total integral expression can be computed with rather high accuracy because the integrand rapidly converges as $1/E'^3$.

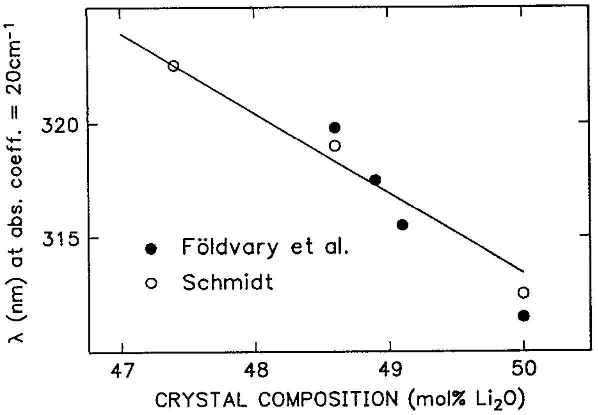

FIG. 5. Shift of the optical absorption edge of lithium niobate with crystal composition. The curve is computed from a Kramers–Kronig analysis.

To test whether this shift in the absorption edge can be described by our generalized Sellmeier equation, we calculated—using the Kramers–Kronig integral as outlined above—which shift should be expected from the variation of the refractive index. The computed curve for extraordinary polarization is shown in Fig. 5 and found to be in good correspondence with experimental data from Földváry *et al.*[4] and Schmidt[22] also plotted.

It should be mentioned, however, that the shift found in the absorption edge for ordinary polarization cannot be calculated with the same accuracy. A further refinement of the model seems to be necessary.

IV. CONCLUSION

With a two term Sellmeier equation it is possible to describe the refractive indices of $LiNbO_3$ over a considerable composition range with excellent accuracy. The calibration curves for several methods for the determination of the Li content which are based on the refractive indices can be derived from our calculations. Only higher order effects like angle phase matching demand an extended description of the refractive indices to obtain higher accuracy. In combination with a Kramers–Kronig analysis the shift in the optical absorption edge can be computed. Excellent agreement is found with the respective experimental data.

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