Isotope effect in anharmonic double-well potentials

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Analysis of EXAFS in YBa₂Cu₃O₇ shows that the axial oxygen O(4), associated with the Cu-O chains, moves in a double-well potential. Optical measurements of the isotope effect in the frequencies of phonons involved in the axial oxygen motion, show an isotope shift smaller than that obtained assuming a harmonic potential. In this work we present an isotope effect study of the excitation frequencies of two anharmonic potentials, the φ⁴ double-well and the Quadratic double-well (QDW) potentials, when the isotopic mass of the axial oxygen is varied. The potential parameters used correspond to YBa₂Cu₃O₇. We have found that both anharmonic effective potentials φ⁴ and QDW are unable to reproduce the experimental values of the isotopic coefficient (frequency shift), suggesting the presence of a different kind of anharmonicity.

Keywords: Anharmonic lattice modes, isotope effect in phonons, high-Tc superconductor oxides

1. Introduction

Studies of the local structure in layered high-Tc superconductor oxides using extended X-ray absorption fine-structure (EXAFS) analysis have found a double equilibrium position for the axial oxygen in these materials [1–3]. This has been interpreted as evidence of a double well potential associated with the motion of this atom [1]. Pair-radial-distribution (PRD) function analysis of pulsed neutron scattering and neutron diffraction data has also shown the existence of two axial oxygen position in Ti-based high-Tc materials [4, 5]. Recent optical studies in YBa₂Cu₃O₇–x [6–8] have shown that under oxygen substitution specific phonons modes associated with the axial oxygen vibrations, i.e., (505 cm⁻¹ Raman active mode [7] and 565 cm⁻¹ Infrared active mode [6]) exhibit isotope shift smaller than that obtained assuming harmonic motion of this atom [7, 8], suggesting again the presence of anharmonic motion of the axial oxygen. From a theoretical point of view, several models suggest that anharmonicity plays an important role in explaining high-Tc superconductivity [9].

In this work we present an isotope effect study of the excitation frequencies of two anharmonic double-well potentials, when the isotopic mass of the axial oxygen is varied. We study the φ⁴ potential and the quadratic double-well (QDW) potential with the potential parameters corresponding to YBa₂Cu₃O₇. Since, analysis of EXAFS data show an asymmetry of ~ 6% in the PRD function of the axial oxygen, we have consider the symmetric and the asymmetric cases for the QDW potential, in order to evaluate the importance of the asymmetry in the potential on the isotope effect. A comparison of the calculated isotope frequency shift for the modes mentioned above with experimental data is also presented.

In Sect. 2 we present the method of calculation of the isotopic coefficient. In Sect. 3 we analyze the results of the calculations and a comparison with experimental data is presented. Finally, in Sect. 4 we present a summary.

2. The method

We solve numerically the Schrödinger equation for the φ⁴ double-well potential and the QDW potential. The φ⁴ potential is commonly used to describe structural transitions in ferroelectrics, this potential is defined as

\[ V_1(x) = a x^2 + b x^4. \]  

(1)

This potential can represent a single-well potential \(a > 0, b > 0\) or a double-well potential \(a < 0, b > 0\). The form...
of the QDW potential is

\[ V_2(x) = \begin{cases} \frac{A(x - x_1)^2}{2} & x \leq 0 \\ \frac{B(x - x_2)^2}{2} & x \geq 0 \end{cases} \]  

(2)

where \( A = B \) for the symmetric case and \( A \neq B \) for the asymmetric case. The separation of the minima in the potentials (\( \Delta x \)) corresponds to the difference of the two relative distances \( \text{Cu}(1)-\text{O}(4) \) observed in \( \text{YBa}_2\text{Cu}_3\text{O}_7 \), which is \( \Delta x = 0.13 \text{ Å} \) as determined from the EXAFS data through analysis of the pair-radial-distribution function [1]. The other parameters of the potentials are determined from a fit of the effective potential wave function of the ground state to the many-body wave function of the ground state obtained from a polaronic model [10, 11]. For the QDW potential we have considered two cases, the symmetric where \( A = B \) and one asymmetric where \( B \) is 5% bigger than \( A \). Since, the structural EXAFS data correspond to the pair Cu(1)-O(4), therefore the mass \( (M) \) entering in the Schrödinger equation is the reduced mass of the pair Cu-O.

To determine the isotopic coefficient of each excited state the mass of the isotope oxygen is varied from 14–20 u. The frequency associated to the transition from the ground state to the \( n \)-th excited state \( (\omega_n) \) is fitted to a function of the reduced mass \((M)\) of the form

\[ \omega_n \sim M^{-\alpha_n} \]  

(3)

where \( \alpha_n \) is the isotopic coefficient of the \( n \)-th excited state. The isotopic shift in the \( n \)-th frequency \( \Delta \omega_n/\omega_n(\%) \) when \( O^{16} \) is substituted by \( O^{18} \) is calculated from

\[ \Delta \omega_n/\omega_n = \frac{\omega_n(O^{16}) - \omega_n(O^{18})}{\omega_n(O^{16})} \]  

(4)

where \( \omega_n(O^{16}) \) and \( \omega_n(O^{18}) \) is the frequency of the \( n \)-th state for \( O^{16} \) and \( O^{18} \) respectively.

3. Results and Discussion

In Figs. 1 and 2 we show the behavior of the isotopic coefficient for the first few excited states of the \( \phi^4 \) double-well potential and the QDW potential. For reference we have included with a horizontal line the isotopic coefficient for the quartic potential \( (\alpha = 2/3) \) in the Fig. 1 and the isotopic coefficient for the harmonic potential \( (\alpha = 1/2) \) in the Fig. 2. Note the different scale for the value of the isotopic coefficient in the Fig. 1 and Fig. 2. In the Table I, the values of the isotopic coefficient for the studied potentials is summarized. In both double-well potentials the largest value of the isotopic coefficient is for the first excited state, and gradually decreases as the energy state is higher with different behavior for each potential. For the \( \phi^4 \) potential the behavior of the isotopic coefficient as a function of \( n \) is non-monotonic, in contrast with the case of the QDW potential where the behavior is monotonic. The isotopic coefficient converges gradually to the value of 2/3 in the case of the \( \phi^4 \) potential and to the harmonic value (1/2) in the case of the QDW potential as the energy state is higher, because the harmonic potential is the asymptotic potential of the QDW potential for large
amplitudes, and the quartic potential for the $\phi^4$ double-well potential. From a dimensional analysis of the Schrödinger equation it is easy to show that the isotopic coefficient of the quartic potential is $\alpha = 2/3$. The asymmetry of 6% in the QDW potential produces a small change in the isotopic coefficient values (see figure 2), however this change is not the same for all excited states. The largest change found was for the second excited state $\sim 7\%$ with respect to the symmetric case, therefore the asymmetry in the potential has not an important effect on the isotopic coefficient.

In Table II we present the calculated value of the isotope frequency shift ($\Delta \omega/\omega$) for the states 2 and 3 when the isotopic mass of oxygen is changed from $O^{16}$ to $O^{18}$, these modes correspond to the Raman and infrared active modes observed experimentally at $\sim 500 \text{ cm}^{-1}$ and $\sim 570 \text{ cm}^{-1}$ respectively. The experimental value of the isotope frequency shift and the result from the shell model (harmonic) for these two modes are also presented [6–8]. We can see that the calculations of the isotope shifts using rigid double-well potentials differ from the experimental values even more than those found using the shell model (harmonic potentials). Therefore, both anharmonic potentials $\phi^4$ and QDW are unable to reproduce the experimental values of the isotopic coefficient (frequency shift) despite that these potentials reproduce the local structure observed with EXAFS [1]. This result suggests the presence of a different kind of anharmonicity in the dynamic of the axial oxygen, possibly polaronic behavior [12].

4. Summary

We have calculated the isotopic coefficient for the first few excited states of two anharmonic potential, the $\phi^4$ double-well potential and the QDW potential, when the isotopic mass of oxygen is varied from 14–20 uma. For all excited states the isotopic coefficient differs from the harmonic value as is expected in anharmonic potentials, however it approaches the limiting value of 2/3 in the case of the $\phi^4$ potential and to the value of 1/2 in the case of the QDW potential for high energy states. Both anharmonic potentials $\phi^4$ and QDW are unable to reproduce the experimental values of the isotopic coefficient (frequency shift), suggesting the presence of a different kind of anharmonicity like polaronic behavior.

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