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Physica B 368 (2005) 287–296
PHYSICA B
www.elsevier.com/locate/physb

Modeling of the lattice dynamics in MgO crystals with point defects in different charge states

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Received 28 January 2005; received in revised form 12 May 2005; accepted 12 May 2005

Abstract

The lattice dynamics of MgO crystals having vacancies and hydrogen impurities in different charge states was simulated in terms of a shell model using the recursive method with symmetry considerations. Models of electron centers (displacement of ions and the distribution of the electron density in the defect region) were discussed in detail. Information about frequencies of defect-induced resonance and local vibrations of different symmetry types was obtained.

PACS: 63.20.Dj; 63.20.Pw

Keywords: Localized modes; Point defects; Lattice dynamics

1. Introduction

Metal oxides, including MgO, are very significant for engineering applications as a parent material of optical devices, fibers, sensors, etc. [1–3]. The main intrinsic defects in MgO crystals are oxygen vacancies in different charge states: a neutral vacancy, a vacancy trapping one electron (an F^+-center), and a vacancy trapping two electrons (an F-center).

Many optical characteristics of crystals are related to dynamic processes at electron centers. One of these significant processes in wide-gap oxides is the photoconversion of F- and F^+-centers. It was shown experimentally [4,5] that hydrogen ions and OH^- complexes play a considerable role in photoconversion processes. For example, the $F \rightarrow F^+$ photoconversion involving hydrogen ions is observed in thermochemically colored MgO crystals [4].

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doi:10.1016/j.physb.2005.05.052

The experimental observation of dynamic and relaxation processes at electron centers presents a difficult task since these processes are pico- or femtosecond long. The correct description of electronic processes (relaxation, electron transitions, etc.) and the photoconversion of F-like centers requires information about localized vibrations induced by these centers and hydrogen ions in different charge states.

Theoretical calculations of dispersion curves and the density of single-phonon states in ideal MgO crystals were compared with relevant experimental data in a number of papers, e.g. [6,7]. The dynamics of the magnesium oxide crystal lattice containing vacancies has not been studied so far. The study [4], which deals with experiments on local vibrations of H^- and H^{2-} ions in thermochemically colored MgO crystals, deserves mentioning among studies concerned with vibrations in MgO crystals containing hydrogen impurities.

A limited number of Refs. [8–13] is available reporting experimental and theoretical studies of the vibration structure of vacancies and F-centers in dielectric crystals. For example, gap vibrations of F-centers in alkali-halide crystals were measured in Refs. [8–10]. Researchers [11,12] performed theoretical calculations of gap and resonance vibrations induced by F-centers in KI and KCl crystals. Results of those calculations agree well with relevant experimental data. Information about localized vibrations of F-centers in SrF_2 crystals [13] and neutral vacancies in CaF_2 [14] and Si [15] crystals was also obtained using calculation methods. The main conclusion, which can be drawn from the aforementioned studies, is that numerical values of frequencies and the number of resonance vibrations, which are due to the presence of vacancies, are determined by specific features of the atomic structure of crystals, the type of chemical bonds and the vacancy charge. Detection and analysis of resonance vibrations of defects require complicated experiments or calculations. Information about localized vibrations in oxides, which are induced by vacancies in different charge states, is unavailable in the literature. The literature covers in more detail resonance and local vibrations of hydrogen ions in dielectric crystals. For example, the treatises [16,17] review experimental and theoretical studies of local vibrations of hydrogen ions in alkali-halide and alkaline-earth fluoride crystals. However, resonance and local vibrations of hydrogen ions in different charge states in dielectric crystals, including MgO, have not been simulated up to date.

The correct calculation of vibration spectra in MgO crystals with F-like centers requires information about displacements of ions and the electron density distribution in the defect region. The lattice relaxation and the charge distribution near F-like centers in crystals depend on specific features of the electronic structure of these centers. The electronic structure of F-like centers in MgO has been studied well in terms of various theoretical models [18–24].

These defects are most frequently described using a hydrogen-like model [18], which explains qualitatively the appearance of local electron states (s- and p-type) in the forbidden gap in an ideal crystal. The main difficulties encountered in the qualitative description are due to the fact that the wave function of a defect is a widely distributed one. However, it is very important to consider distortions induced by a defect, as acknowledged in all studies dedicated to modeling of F-like systems [18–24]. The difference between results of calculations, which have been performed to date, consists in the position of the ground state of a defect relative to the valence band in crystals, the position of excited and relaxed excited states of a defect relative to the conduction band, and the magnitude and the character of the lattice distortion caused by a defect.

The most accurate results have been obtained so far using embedded cluster models [21–24], which employ a quantum-chemical method for description of the electronic structure of the defect itself and its nearest environment and a molecular statistics method [25] for description of the lattice relaxation and polarization of crystal regions located far from the defect. Unfortunately, dimensions of the chosen supercells were inadequate for accurate non-empirical methods [20]. The semi-empirical Hartree–Fock method was used [25] to simulate the electronic structure. Results of analogous calculations, which were based on the