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Electric-field gradients at [181]Ta impurity sites in Ho$_2$O$_3$ and Eu$_2$O$_3$ bixbyites

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Abstract

The time-differential γ–γ perturbed-angular-correlation (PAC) technique with ion-implanted [181]Hf tracers has been applied to study the hyperfine interactions of [181]Ta impurities in the cubic bixbyite structure of Ho$_2$O$_3$ and Eu$_2$O$_3$. The PAC experiments were performed in air in the temperature range 300–1373 K (in the case of Ho$_2$O$_3$) and 77–1273 K (in the case of Eu$_2$O$_3$). For both oxides, two electric-quadrupole interactions were found and attributed to the electric-field gradients (EFGs) acting on [181]Ta probes substitutionally located at the two free-of-defects nonequivalent cation sites of the bixbyite structure. In the case of Ho$_2$O$_3$, two additional interactions were found in the temperature range 300–573 K. These results, as well as previous characterizations of the EFG at [181]Ta sites in bixbyites, were compared to those obtained in experiments using [111]Cd as probe, and to point-charge model calculations. Very recent *ab initio* predictions for the EFG tensor at impurities sites in binary oxides are also discussed. All these results enable us to discuss the validity of the widely used ionic model to describe the EFG in these highly ionic compounds.
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1. Introduction

Perturbed-angular correlations (PAC) and other hyperfine interaction measurements are widely used experimental techniques that provide local information on the interaction of a probe-nucleus with the surrounding electronic charge distribution [1]. An interpretation of such measurements can lead to a detailed knowledge of structural, electronic, and magnetic properties of a solid (see e.g., Ref. [2]). One of the measured quantities, the nuclear-quadrupole frequency ω_Q, is proportional to the major principal component (V_{33}) of the electric-field gradient (EFG) tensor. Due to the EFG's r^{-3} dependence on the distance from the probe-nucleus to the charge sources, the EFG "felt" by the nucleus reflects sensitively the non-spherical electronic charge distribution around this nu-

cleus. Therefore, the EFG is one of the most important clues for the understanding of the electronic structure in solids and the nature of the chemical bonding.

Usually, the probe-atom is an impurity dopant, which is present in either trace or small amounts in the host crystal. For this reason, interpreting experimental EFG results involves the understanding of chemical differences between the probe atom and the indigenous ion replaced by the impurity. The experimental results show that the differences between probes and indigenous atoms are manifest in subtle ways that are not well described by simple models, as already pointed out in Ref. [3]. For an accurate calculation of the EFG, the electronic configuration of the host, perturbed by the presence of the impurity, has to be determined. This can be done in the framework of the density-functional theory (DFT). In this kind of calculation, electronic and structural effects introduced in the host by the presence of the impurity probe (impurity levels, structural distortions, etc.) can be described without the

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use of arbitrary suppositions. Unfortunately, these calculations prove to be not trivial and time consuming. For this reason, very few EFG calculations have been performed in systems with impurities and the method is far from being routinely applied in this field [4]. Alternatively, in the case of mainly ionic compounds, the very simple point-charge model (PCM) has been currently used for the interpretation of the experimental EFGs [5]. But in this model, charge-transfer effects are only crudely estimated and covalence and the impurity character of the probe are completely neglected. Additionally, corrective factors (like the antishielding Sternheimer factor γ_∞) must be used in this framework in order to account for the core polarization of the probe-atom. Therefore, it is important to study the conditions under which the PCM can be used as well as its limitations.

In this work, we report PAC experiments using ^{181}Ta as probe in the bixbytes Eu_2O_3 and Ho_2O_3 in order to complete the systematic study of the EFG at ^{181}Ta atoms located at defect-free cation sites in the bixbyite structure. This systematics is compared to those previously established for the ^{111}Cd probe and to PCM predictions, and discussed within the framework of recent *ab initio* EFG calculations in binary oxides. From our results it is clear that the problem of the EFG at impurities in bixbytes cannot be described by the ionic model and that the impurity character of the hyperfine probes should not be neglected in a proper theoretical description of electronic properties of doped oxides.

2. Sample preparation, measurements and results

Fe, Mn, Sc, In, Tl, Y, and the rare-earth elements, under suitable conditions, form a sesquioxide. Polymorphism is common and below about 2300 K, three polymorphous crystallographic structures have been found: the hexagonal-A, monoclinic-B, and cubic-C form (bixbyite) [6]. In the cubic form, the cations form a nearly cubic face-center lattice (space group Ia3) in which six out of the eight tetrahedral sites are occupied by oxygen atoms. The unit cell of the crystal structure of these oxides consists of eight such cubes, containing 32 cations and 48 O^{-2} ions. Two nonequivalent cation sites, called "C" and "D", both with 6-fold oxygen coordination, characterize the structure. Their relative abundance in the lattice is $(f^C f^D) = 3$. Site D is axially symmetric and can be described as a cation surrounded by six oxygen atoms at the corners of a distorted cube, leaving two corners of the same diagonal free (D_{3d} point-group symmetry). In site C (C_2 point-group symmetry) the cube is more distorted and the six oxygen atoms leave free two corners on a face diagonal (see Fig. 1). Therefore we expect two clearly distinguishable hyperfine interactions. That corresponding to site C will be characterized by an asymmetry parameter $\eta^C \neq 0$, while $\eta^D \approx 0$ will characterized that corresponding to site D. According to their relative abundances, the first one should be present with more intensity.
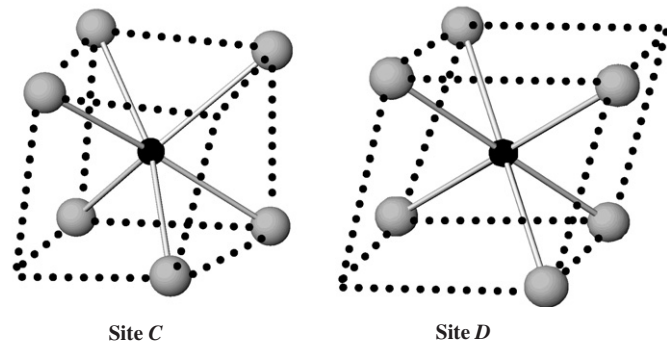

Fig. 1. Nearest-neighbor oxygen distribution around each cationic site C and D (black atoms) in the bixbyite structure.

In order to prepare the PAC samples, commercially obtained high-purity Ho_2O_3 and Eu_2O_3 powders (Aldrich Products, 99.9% and 99.95% metallic purity, respectively) were treated in air for 24 h at 1023 K in order to achieve the crystalline C-phase and then pressed as circular pellets. Afterwards, the Ho_2O_3 pellet was sintered in air for 2.5 h at 1273 K, whereas Eu_2O_3 was sintered under similar conditions but at 1123 K for 1.5 h. In both cases, powder XRD analyses of the samples performed before and after the sintering showed that only the C-phase was present and also revealed an increase in the crystallinity of the samples. The ion accelerator of the ISKP, Bonn, was then used to implant ^{181}Hf ions into the samples with energies and doses of 160 keV and 5×10^{13} ions/cm^2 in the case of Ho_2O_3, and 155 keV and 5×10^{13} ions/cm^2 in the case of Eu_2O_3. In order to perform the experiments presented in this work we made use of the well-known 133–482 keV γ–γ cascade of ^{181}Ta, produced after the β^- nuclear decay of ^{181}Hf. The PAC experiments were performed using four BaF$_2$ detectors in a coplanar 90° arrangement and a fast–fast logic coincidence system. The time and energy resolutions of the spectrometer for ^{181}Ta γ-rays were 0.65 ns (full-width at half-maximum of the prompt peak) and 9.5% for γ-rays of 662 keV, respectively. The experimental perturbation functions, $R(t)$, were derived from eight concurrently measured coincidence spectra, four taken between detectors positioned with 180° symmetry and four with 90° symmetry [7]. To analyze the measured perturbation functions we used a multiple-site model for nuclear–electric-quadrupole interactions, polycrystalline samples, and spin $I = 5/2$ intermediate level:

$$R(t) = A_{22}^{exp} G_{22}(t) = A_{22}^{exp}$$
$$\times \sum_i f^i \left(S_{20,i} + \sum_{n=1}^{3} \left[S_{2n,i} \cos(\omega_{n,i}t) e^{-\delta_i \omega_{n,i} t} \right] \right), \quad (1)$$

where f^i is the relative fraction of nuclei that experiments a given perturbation. The ω_n interaction frequencies are related to the nuclear-quadrupole frequency $\omega_Q = eQV_{ZZ}/40\hbar$ by $\omega_n = g_n(\eta)\omega_Q$. The g_n and S_{2n} coefficients are known functions [8] of the asymmetry parameter $\eta = (V_{XX} - V_{YY})/V_{ZZ}$, with V_{ii} the principal EFG tensor