

Application of perturbed angular correlations to oxides

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Abstract

Nearly all elements can be oxidized and develop oxides, often with different oxygen contents and in different crystalline phases. Applying the classical perturbed angular correlation (PAC)-probes $^{111}\text{In}/^{111}\text{Cd}$ or $^{181}\text{Hf}/^{181}\text{Ta}$, the probes are usually found on unperturbed cation lattice sites surrounded by oxygen atoms. Using different oxides of the same structure or comparing different crystal classes the position of the oxygen neighbours near the probe can be varied in a wide range. This allows testing theoretical concepts of electric field gradient (EFG) calculation.

In general, the melting point of an oxide is very high, and the PAC experiments span a huge temperature range from $T_m = 10$ to 1700 K. Two temperature regions are known, where $^{111}\text{In}/^{111}\text{Cd}$ probes show dynamic hyperfine-interactions, which occur when the EFG changes direction or strength during the lifetime of the probe. At low temperatures the electron capture “after-effect” is observed, caused by a low availability of charge carriers in semiconducting or isolating oxides. At very high temperatures intrinsic defects or mobile atoms in ternary oxides move so fast, that undamped perturbation functions arise.

Realizing the big impact of STM and AFM to the surface science, a probing technique like PAC for the next neighbours *inside* a sample seems to be attractive. In the past, numerous discussions asked whether the inserted PAC-probes are really spies—only observers—or if they actually change that neighbourhood, that they are supposed to analyse. Distortions in oxides are discussed.

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1. Introduction

Probing the local structure of a solid by perturbed angular correlations (PAC) essentially depends on the knowledge of the lattice site where the probe is placed. Nearly all elements can be oxidized and develop oxides, often with different oxygen contents and in different crystalline phases. Introducing the classical PAC-probes $^{111}\text{In}/^{111}\text{Cd}$ or $^{181}\text{Hf}/^{181}\text{Ta}$, they are usually found on unperturbed cation lattice sites surrounded by oxygen atoms. In consequence, a big amount of PAC-experiments used this playground to find or test the correlation between the crystallographic geometry and the electric field gradient (EFG) parameters in oxide-families of similar structure. Today this large body of experimental data on EFGs in

different oxide crystal-classes allows for comparison with theoretical predictions. A key role belongs to binary and ternary oxides, where In- and Hf-cations are part of the compound. In such a case no doubts arise about the site of the probe.

Usually, oxides are in equilibrium with the atmospheric oxygen. Oxygen uptake and non-stoichiometry are the consequences, as well as phase transitions. All these phenomena are typical topics for PAC-experiments and they occur on oxide samples during timescales of hours or days. Of similar importance is the case of very short timescales. Here the EFG may change its direction or strength during the lifetime of the probe, and the so-called “dynamical interaction” takes place. As an example, two temperature regions are known, where $^{111}\text{In}/^{111}\text{Cd}$ probes show this dynamic hyperfine-interactions. At low temperatures the electron capture (EC) “after-effect” (AE) is observed, caused by a low availability of charge carriers in

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semiconducting or isolating oxides. At very high temperatures intrinsic defects or mobile atoms in ternary oxides move so fast, that undamped EFGs arise.

Realizing the big impact of STM and AFM to the surface science, a probing technique like PAC for the next neighbours *inside* a sample seems to be attractive. But numerous discussions in the past asked whether the inserted PAC-probes are really spies—only observing—or if they actually change the neighbourhood that they are supposed to analyse. Already old point-charge model (PCM) calculations gave hints to distortions of the lattice by the probe atoms, and today the *ab initio* calculations with the density-functional theory clearly depend upon them. In rare cases, a direct and independent experimental evidence of a modified lattice position exists from emission-channelling experiments, as for $^{111}\text{In}/^{111}\text{Cd}$ probes in Cr_2O_3 .

Finally, it should be mentioned, that the important aspect of ferro- or anti-ferromagnetism in oxides is omitted in this paper. The PAC technique, described in several articles and textbooks [1–3] will also not be explained here.

2. Structural aspects

2.1. Binary oxides and $^{111}\text{In}/^{111}\text{Cd}$ probes

The first oxide ever investigated by the PAC technique was In_2O_3 , the native oxide of the ^{111}In probes. Already in the year 1964 Salomon [4] identified the “electron capture after-effect”, which is still the topic of Chapter 3.1. And it took nearly 20 years to identify the two EFGs, which are the signature for probes on the two non-equivalent cation sites (called D and C) of the cubic bixbyite structure of this oxide [5]. The probes reside at the centre of two oxygen octahedra with quite different geometry and cation-oxygen bond-length. Furthermore, the crystallographic abundance is well reproduced by the observed fractions of different EFGs [5,6]. The method of introducing the ^{111}In probes (during the chemical synthesis, by implantation or diffusion) does not change the general result: evidently the radioactive probes find the correct crystallographic sites in their “own” oxide. Among the binary oxides, there are more sesquioxides that crystallize in the same bixbyite structure having lattice constants in a wide range from 0.94 to 1.09 nm. As these oxides show nearly pure ionic binding [7] the naïve PCM was applied to calculate the EFG at the two sites C and D. In this model the strength of an EFG is expected to be proportional to d^{-3} , where d represents a typical distance to a neighbouring charge. Therefore, the group of bixbyite oxides gave a unique chance to study the influence of the lattice size on the observed EFG [8]. As shown in Fig. 1 the measured quadrupole frequencies ν_Q on both sites scale nearly linearly with a^{-3} (a = lattice constant) in the whole bixbyite crystal-class [9]. In more detail, the following information on the local structure can be obtained: For site D, the deviation from the linearity of ν_Q^D with a^{-3} is small and axial symmetry ($\eta^D = 0$) is

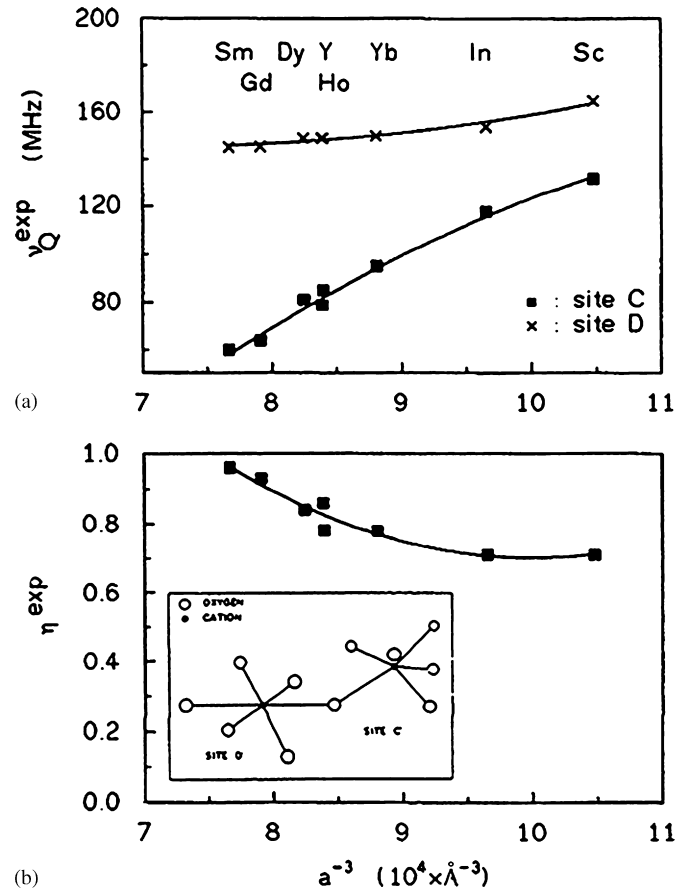


Fig. 1. (a) The dependence of the hyperfine parameters ν_Q for $^{111}\text{In}/^{111}\text{Cd}$ probes on both sites D and C of the bixbyite structure on a^{-3} , where a is the lattice constant. (b) The asymmetry parameter $\eta(D)$ varies slowly with a^{-3} , whereas $\eta(C) = 0$ remains for all bixbyites [9].

observed for all oxides. For site C a dramatic non-linear increase of ν_Q^C and decrease of η^C with a^{-3} is found. The clear interpretation is that the octahedra around site D remain regular through the bixbyite series, while the irregular octahedra around site C are increasingly deformed with increasing lattice constant. To that time the PCM seemed to allow a reasonable calculation and interpretation of the observed EFGs.

After these promising results in the bixbyite oxides a similar attempt was done with other binary-oxide families. This changed the distortion and size of the oxygen octahedra, but varied also the oxygen coordination number to four (f.e. CuO) or two (e.g. Cu_2O). As the result of these experiments, a large data set of EFGs was obtained for $^{111}\text{In}/^{111}\text{Cd}$ probes on the cation-sites of binary oxides. The Göttingen-group compared all results with PCM calculations. Their overview for the binary oxides is given in Fig. 2a [10]. The measured frequencies ν_Q (exp) are divided by the result of the PCM calculations. For each oxide/site the ratio $\beta(\text{exp}) = \nu_Q(\text{exp})/\nu_Q(\text{PCM})$ is plotted versus the bond-length $\langle d \rangle$ averaged over all next-neighbour oxygen ions. Most data with $\langle d \rangle \geq 2.1 \text{\AA}$ are found within the range

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