IN SITU PROBING OF ELECTRONIC SURFACE STRUCTURE IN IONIC CRYSTALS BY RESONANT SECOND HARMONIC GENERATION

J. Reif, P. Tepper, O. Semmler, E. Matthias

To cite this version:
J. Reif, P. Tepper, O. Semmler, E. Matthias. IN SITU PROBING OF ELECTRONIC SURFACE STRUCTURE IN IONIC CRYSTALS BY RESONANT SECOND HARMONIC GENERATION. Journal de Physique Colloques, 1987, 48 (C7), pp.C7-733-C7-735. <10.1051/jphyscol:19877180>. <jpa-00227005>

HAL Id: jpa-00227005
https://hal.archives-ouvertes.fr/jpa-00227005
Submitted on 1 Jan 1987

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
IN SITU PROBING OF ELECTRONIC SURFACE STRUCTURE IN IONIC CRYSTALS BY RESONANT SECOND HARMONIC GENERATION

J. REIF, P. TEPPER, O. SEMMLER and E. MATTHIAS

Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33, F.R.G.

Abstract

Resonant second harmonic generation at the surface of transparent ionic crystals is used to investigate the electronic properties of these surfaces. We report on in situ measurements on barium fluoride, sodium chloride, and potassium chloride in air. From the divalent crystal, the second harmonic signal should be mainly due to surface dipole interaction, since it shows spectral resonances and the dependence on azimuthal crystal orientation reflects the surface symmetry. From the monovalent crystals, the purely surface signal does practically not depend on the azimuthal crystal orientation, and should hence be due mainly to long range interaction. If one component of the light polarization is perpendicular to the surface, a surprising asymmetry is found in the signal from the alkali salts.

Second harmonic generation (SHG) in reflection from the surface of centrosymmetric media is, in principle, a promising tool for investigating electronic surface structure /1/. Since it represents a purely optical method, it is not restricted to a special environment such as ultra-high vacuum. Hence, it provides a way of in situ, non destructive, and remote measurement of surface properties. It can be shown, following the argument of Bloembergen et al. /2/, that any higher multipolar contributions to the signal from the bulk should vanish, if both fundamental and second harmonic are polarized perpendicular to the plane of incidence (i.e. the respective electrical field vectors are parallel to the surface and to each other) /3/. So, under this condition, the process is highly surface sensitive. Guyot-Sionnest and Shen /1/ have demonstrated that the signal should be due to long-range in surface electric quadrupole interaction and to local electric dipole terms. The latter are attributed to local electronic excitations in the interface layer. From our cluster calculations /3/ we expect such states at the BaF$_2$ (111) surface. Indeed, we observe a spectral dependence of the second harmonic signal, as is shown in fig. 1.

Figure 1 Reflected second harmonic intensity from a polished BaF$_2$ (111) surface as a function of dye laser wavelength (coumarine 152). Both fundamental and second harmonic wave are polarized perpendicular to the plane of incidence (s-polarization). The angle of incidence is 45°. The azimuthal orientation of the crystal was not measured.

This means that at least part of the electronic surface structure is preserved despite the fact that the surface is obviously covered with adsorbates from the surrounding air. Apparently, to a great extent the signal can be associated with the
Figure 2. Azimuthal dependence of the second harmonic signal from BaF$_2$ (111) (radius) projected onto the surface structure (fundamental at 532 nm), when the crystal is rotated about its normal. a) s-polarization, b) p-polarization. Angle of incidence: 45°.

Figure 3. SHG from BaF$_2$ (111) as a function of laser wavelength for 45°-polarization. a) Azimuth for maximum signal. b) Azimuth rotated by 30° relative to a). c) Azimuth rotated by 60° relative to a).

Figure 4. SHG from NaCl (111), at 532 nm. Azimuthal dependence for a) s-polarization, b) 45°-polarization.
dipole interaction. Having an ionic crystal, we can identify macroscopic dipolar azimuths in the surface plane. These are along the barium-fluorine directions. Due to the $C_3$ symmetry of the (111) plane and the fact that all polarizations are parallel to the surface, this leads to a sixfold symmetry of the second harmonic gain, if the crystal is turned about the surface normal. The projection of the observed symmetry onto the structure of the (111) surface in Fig. 2a confirms this argument. If, however, we change the light polarizations such that there is a component pointing normal to the surface, the azimuthal dependence of Fig. 2b is obtained. This distribution may be described by adding an isotropic term to the second harmonic field amplitude $E_{\text{SH}} = A + B \sin(3\psi)$, i.e.

$$E_{\text{SH}} = A + B \sin(3\psi)$$

with $\psi$ being the azimuthal angle. The spectral dependence of SHG with a polarization component perpendicular to the surface is shown in Fig. 3 for both E-vectors being at 45° to the plane of incidence. This is the situation where the total signal is strongest. The principal feature of the spectrum, i.e., two peaks around 510 nm and 535 nm, is similar to s-polarization, however, the relative intensities are different. This might come from a different azimuthal orientation in both cases, as can be seen from the difference between Fig. 3a and b. Work is presently going on in our laboratory, to investigate this question in more detail.

We also performed first experiments on monovalent ionic crystals (NaCl and KCl). Here, we do not expect to find the pronounced electronic structure in the bandgap at the surface. Consequently, surface SHG should be dominated by the long-range electric quadrupole term more likely than by dipole interaction. This means, that no pronounced influence of the microscopic ordering should be present. Indeed, for s-polarization we observe nearly azimuthal isotropy for both crystals. This is shown in Fig. 4 for NaCl. For 45°-polarization, however, we observe a tremendous one fold anisotropy in both cases. Presently, we do not yet understand this result, but our feeling is that it might be associated to some effect of adsorbed water. This is subject to further investigations.

Acknowledgements

We thank H. Schmelz for participation in part of the NaCl and KCl measurements. This work was supported by the Deutsche Forschungsgemeinschaft, Sfb 6, and Kali und Salz AG (NaCl and KCl).

References


/3/ J. Reif, H.B. Nielsen, O. Semmler, P. Tepper, and E. Matthias, E. Westin, and A. Rosen, Resonant Multiphoton Processes in Laser-Surface Interaction, this volume, p 443