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Polarization-modulated infrared reflection difference microspectroscopy: Experiment and model

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ABSTRACT

Polarization-modulated infrared reflection difference microspectroscopy is a sensitive tool to spatially and spectrally resolve optical anisotropy of micrometric crystalline domains. However, intrinsic artifacts are associated with polarization modulation experiments, in particular due to the wavenumber-dependent efficiency of the photoelastic modulator. Here an account addressing this problem in our experimental approach is given. Comparing data from measurements on $Ca_{1.4}Sr_{0.6}RuO_4$ and $Bi_{0.3}Ca_{0.7}MnO_{3+\delta}$ with model calculations, it is shown that a simple model, which is based on reports in the literature, can be used to describe the experimental results.

1. Introduction

Polarized infrared spectroscopy is a powerful tool to study anisotropy of solid-state materials [1]. Polarization modulation (PM) is a technique that is used to measure small dichroic or anisotropic effects with high sensitivity [2]. The sensitivity of PM stems from the fact that the dichroic difference or reflection difference spectrum is measured directly by modulating the polarization of the incident infrared beam at high frequency (typically several tens of kHz) with a photoelastic modulator. PM infrared spectroscopy has been applied to studies of vibrational circular dichroism [3–6] and vibrational linear dichroism [2,3,7–18] as well as in infrared reflection–absorption spectroscopy [19–25].

Recently, we implemented an experimental scheme using Fourier transform infrared reflection microspectroscopy in combination with polarization modulation and demonstrated its potential to spectrally and spatially resolve anisotropy of solid-state materials in the mid-infrared region [26]. This technique enabled the local probing of charge and orbital ordering-induced anisotropy of a $Bi_{0.3}Ca_{0.7}MnO_{3+\delta}$ crystal [27].

Notwithstanding the capabilities and advantages over conventional static polarization measurements, the PM technique inherently brings about a number of complications. The optical setup and electronic processing used in PM experiments are more involved. More importantly, this method introduces substantial spectral artifacts, in particular due to the wavenumber-dependent efficiency of the photoelastic modulator. Theoretical treatments [3,13] as well as experimental calibration procedures [10,13,20,23] taking account of these artifacts in PM experiments have been reported. With respect to polarization-modulated infrared reflection difference microspectroscopy, the issue of experimental artifacts was touched on previously [26,27]. In this article, an extended account is given, presenting experimental data along with model calculations and discussing the implications of our results.

2. Experimental

The experiments were carried out on the infrared microscope (Nicolet Continuum coupled to a Nexus 870 FT-IR spectrometer) of the beamline IRIS at the electron storage ring BESSY II [28]. The confocal microscopic reflection measurements were performed at atmospheric pressure using brilliant synchrotron radiation, a KBr beam splitter, a 32× Cassegrain objective with a numerical aperture of 0.65, and a liquid-nitrogen-cooled HgCdTe (MCT) detector.

The PM instrumental setup and its implementation in infrared reflection difference microspectroscopy are described in detail elsewhere [26,29,30]. In brief, the setup contains a polarizer (Specac, holographic aluminium grid, KRS-5) and a photoelastic modulator (Hinds Instruments, PEM-90 II, ZnSe, 50 kHz) between the spectrometer and the microscope. In addition to these optical components, it includes electronics that provide modulation control and demodulation (GWC Technologies, synchronous sampling demodulator 100). It is noted that the inherent polarization of the infrared synchrotron radiation is advantageously exploited in the setup [29].

The key component is the photoelastic modulator (PEM) and it serves as the polarization modulation device. By means of piezoelectric transducers the intrinsically optically isotropic PEM crystal

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is periodically stressed by compression and stretching which generates an oscillating birefringence due to photoelasticity. Linearly polarized radiation enters the PEM such that the electric field vector has an angle of 45° with respect to the PEM optical axis. When the peak retardation is one half of the wavelength of the light ($\lambda/2$), the PEM modulates the light beam between two perpendicular, linearly polarized states at its 2nd harmonic (100 kHz). The PEM then acts as an oscillating half-wave plate or polarization rotator [11,31].

Each measurement gives two spectra, the difference spectrum ($I_{diff} = I_{||} - I_{\perp}$) and the sum spectrum ($I_{sum} = I_{||} + I_{\perp}$), where $I_{||}$ and $I_{\perp}$ denote the detected spectral intensities for light polarized in planes parallel and perpendicular with respect to a reference direction. The difference spectrum and the sum background spectrum are acquired simultaneously at the same sample position. Without measuring a reference, the ratio of the difference and the sum spectrum, I_{diff}/I_{sum}, directly yields the normalized experimental reflection difference spectrum, here termed the polarization modulation-reflection difference (PM-RD) spectrum.

3. Results and discussion

3.1. Experiment section

We examined two anisotropic solid-state compounds, $Ca_{1.4}Sr_{0.6}RuO_4$ and $Bi_{0.3}Ca_{0.7}MnO_{3+\delta}$. Fig. 1a shows the absolute reflectivity spectra of the $Ca_{1.4}Sr_{0.6}RuO_4$ *ac* plane optical surface along the metallic *a*-axis and the insulating *c*-axis recorded at room temperature in conventional static polarization measurements. The reflectivity difference amounts to about 60% originating from the two-dimensional crystal structure. The absolute reflectivity spectra of the $Bi_{0.3}Ca_{0.7}MnO_{3+\delta}$ *ac* plane optical surface along the *a*-axis and *c*-axis recorded at 5 °C are given in Fig. 1b. The reflectivity difference is smaller than in the above case, but it still is finite (~10%) which stems from the charge and orbital ordering. It is noted that for each spectrum the subsequent recording of a sample single beam reflection spectrum and a reference gold mirror single beam reflection spectrum was required. In the following, the PM results will be examined relating to these conventionally acquired spectra.

Fig. 2a shows two PM-RD spectra of the $Ca_{1.4}Sr_{0.6}RuO_4$ *ac* plane optical surface. They represent the extremal reflection differences, obtained by rotating the sample by 0° and 80° around the axis normal to the surface.[1] The spectra were recorded in about 30 s at a spectral resolution of 4 cm^{-1} with a 40 × 40 μm^2 aperture, with the $\lambda/2$ peak retardation of the photoelastic modulator set for 2000 cm^{-1}. The spatial resolution in the measurements was found to be adequate to map or distinguish micrometric anisotropic domains with different crystallographic axes in multi-domain crystalline samples [26,27]. The obtained spectra have peculiar spectral shapes, resembling sinusoidal oscillations that decay towards higher wavenumbers and that have multiple arches and nodes. Fig. 2b presents the two extremal PM-RD spectra of the $Bi_{0.3}Ca_{0.7}MnO_{3+\delta}$ *ac* plane optical surface, recorded at angles of 0° and 90° with respect to the *a*-axis in the *ac* optical surface [27]. It is noted that the PM-induced sinusoidal behavior over the spectral range is different from Fig. 2a. This is due to a different maximum PEM birefringence [13], where in this case the $\lambda/2$ peak retardation was set for 3000 cm^{-1}. Also, the observed reflection difference is smaller than in Fig. 2a, as is expected (cf. Fig. 1).

Considering the reflectivity spectra shown in Fig. 1a and b which exhibit a rather flat response, one can expect that the reflectivity differences would be also monotonically varying in this frequency range. However, the PM-RD spectra, shown in Fig. 2a and b, exhibit large oscillations with changing signs. This artifact arises from the polarization modulation [3,13]. Intrinsically, there exists a wavenumber-dependent modulator efficiency, i.e., a wavenumber-dependent phase retardation amplitude. Only at the wavenumber $\bar{\nu}_{\lambda/2}$ where $\lambda/2$ peak retardation arises and hence linear polarization

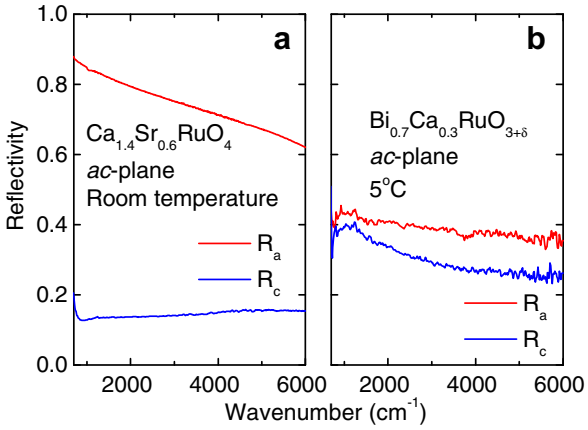

Fig. 1. (a) Absolute reflectivity spectra of the $Ca_{1.4}Sr_{0.6}RuO_4$ *ac* plane optical surface along the metallic *a*-axis and the insulating *c*-axis recorded at room temperature in conventional static polarization measurements. (b) Absolute reflectivity spectra of the $Bi_{0.3}Ca_{0.7}MnO_{3+\delta}$ *ac* plane optical surface along the *a*-axis and *c*-axis recorded at 5 °C.

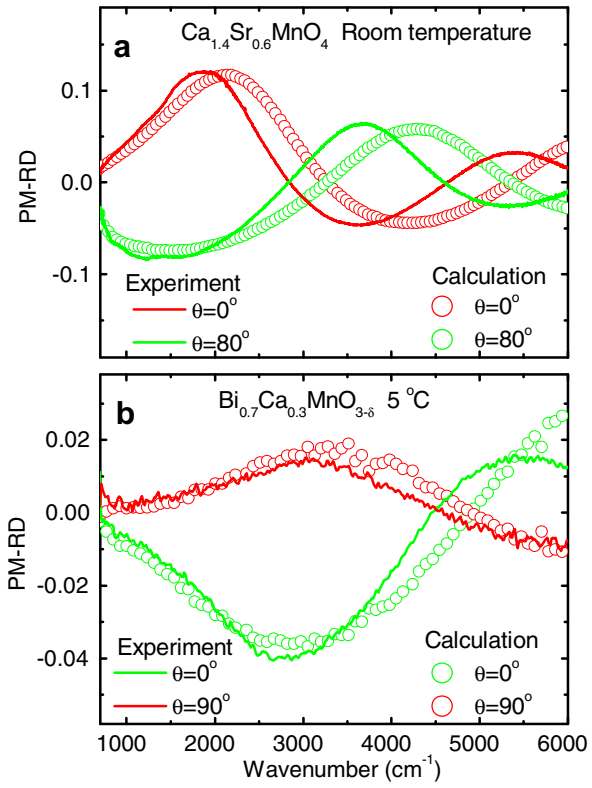

Fig. 2. (a) PM-RD spectra of the $Ca_{1.4}Sr_{0.6}RuO_4$ *ac* plane optical surface, recorded at angles of 0° and 80° around the axis normal to the surface. (b) PM-RD spectra of the $Bi_{0.3}Ca_{0.7}MnO_{3+\delta}$ *ac* plane optical surface, recorded at 5 °C at angles of 0° and 90°. The calculation results using the fit parameters *g* and γ (see Table 1) are shown as open circles.

[1] The extremal values are expected to occur at 0° and 90°. The observed deviation may be due to a slight tilting of the sample surface with respect to the optical axis of the objective. This can lead to a change of the γ value upon sample rotation by changing the optical path of the reflected light.