

## Dispersion analysis of non-normal reflection spectra from monoclinic crystals

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### ABSTRACT

Results of the first dispersion analyses of polarized reflection spectra from a monoclinic  $a$ - $c$  crystal plane taking properly into account the monoclinic symmetry and non-normal incidence on the crystal surface are reported. Spectra were recorded for the incidence angles  $\alpha = 8^\circ, 16^\circ, 40^\circ$  and  $60^\circ$ , and for each at four different polarization angles. For the first two incidence angles the spectra were additionally analyzed under the assumption of normal incidence and the results were compared to those which resulted from the exact treatment. The comparison focused on two different aspects. The first aspect concerns the validity of the oscillator parameters. Accordingly, oscillator parameters of IR active modes obtained by dispersion analysis under the assumption of normal incidence do not show systematic errors despite the simplified treatment. This is a consequence of the fact that errors due to the incorrect assumption of normal incidence are compensated mainly by increases of the diagonal terms of the high frequency dielectric tensor. The corresponding values obtained under the assumption of normal incidence show averaged standard deviations of about 2% at  $8^\circ$  and about 9% at  $16^\circ$ . The second aspect investigated focuses on the employment of the oscillator parameters to generate the dielectric function tensor for optical calculations. Here we found that, as a direct consequence of the increased high frequency dielectric tensor, errors substantially increase if the resulting dielectric tensor functions are employed to calculate the reflectance at higher angles of incidence. Therefore, and since the increase of computational effort due to the exact treatment is small, we strongly suggest and encourage its use instead of the simplified treatment.

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### 1. Introduction

In 1972 Berreman provided a  $4 \times 4$  matrix formalism based on which it is possible to calculate reflectance for arbitrary incidence from anisotropic layer stacks and crystals provided their dielectric tensor function is available [1]. In principle this formalism can also be used for dispersion analysis (DA) based on reflectance spectra from crystals with low symmetry. Instead of employing Berreman's formalism and simplifying it for normal incidence and special geometries, own formalisms were developed shortly thereafter for monoclinic [2–4] and somewhat later for triclinic single crystals [5], all under the constraint of normal incidence and for the former under the additional constraint of incidence on the  $a$ - $c$  crystal plane. The development and employment of these formalisms was justified as the computational effort for Berreman's formalism

in its general form is comparably high. Despite the enormous progress over the last decades computers were subjected to, even nowadays the speed increase by a factor of about 5 employing the reflectance formalisms for monoclinic crystals under normal incidence on the  $a$ - $c$ -crystal plane is still highly welcome. This is due to the fact that the reflectance has to be calculated over a certain spectral range for several spectra (at least 3) in parallel and that this calculation has to be carried out repeatedly for many iterations of the fitting process until a satisfying agreement between measured and calculated spectra is obtained.

The simplification of the formalisms for monoclinic crystals, however, is only partly a result of assuming normal incidence. The major contribution to the simplification is based on employing the  $a$ - $c$ -crystal plane for reflectance measurements. At this special orientation the dielectric tensor is block-diagonalized and consists of a  $2 \times 2$  matrix and a scalar complex function  $\epsilon_b$ , the reflectance from the  $a$ - $c$  crystal plane is no function of  $\alpha$  as long as the incident light is  $s$ -polarized. The  $2 \times 2$  matrix cannot be diagonalized for the real and the imaginary part at the same time, which is a consequence of the transition moments in the  $a$ - $c$  crystal plane being no longer bound to axes of rotation, a symmetry element which exists in monoclinic crystals only along the  $b$ -axis.

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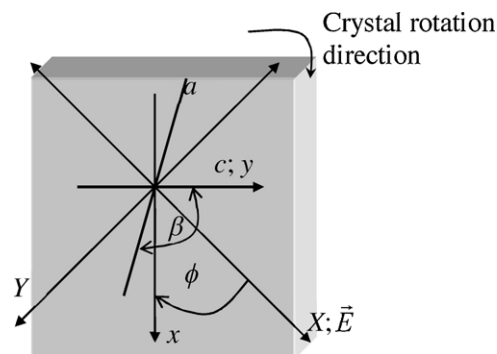
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Recently we investigated how a combined  $4 \times 4$  matrix formalism [6] based on those developed by Berreman [1] and Yeh [7] is simplified under the constraint of reflectance from the monoclinic  $a$ - $c$ -plane. We found that the result is only marginally more complex than that obtained under the additional assumption of normal incidence [8]. Accordingly, the computational speed increase based on the assumption of reflectance from the monoclinic  $a$ - $c$ -plane is given by a factor of 4.5 compared to Berreman's general formalism without any simplifications concerning the reflecting crystal plane or the angle of incidence. This factor is only slightly further improved to 4.6 assuming additionally normal incidence. Based on this result, namely the 0.1 increase in the speed, we concluded that the non-normal incidence can now be properly accounted for. It is worth mentioning that truly normal incidence is experimentally complex to realize and needs the employment of a beamsplitter [9,10]. Therefore the vast majority of measurements has been taken at non-normal incidence including most correctly carried out dispersion analyses on monoclinic crystals [11–22]. In these studies the applied angles of incidence ranged from  $5^\circ$  to  $16^\circ$ .

In this paper we investigate the errors introduced by assuming normal incidence for the evaluation of spectra taken from the monoclinic  $a$ - $c$ -plane at  $8^\circ$  and  $16^\circ$  for the particular example of  $\text{K}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , a system the mid-IR reflectance spectra of which have already been studied previously [18]. We decided to use  $\text{K}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  as it comprises a comparably large number of oscillators with representative characteristics and since its vibrational and reflectance characteristics were well known to us.

In addition to angles of incidence of  $8^\circ$  and  $16^\circ$ , sets of reflectance spectra were also recorded at  $40^\circ$  and  $60^\circ$ . All four sets of spectra were subjected to a DA taking properly into account non-normal incidence. The results were cross-checked for consistency to evaluate their validity. Additionally, DA on the sets consisting of four spectra recorded at different polarization angles, obtained at  $8^\circ$  and  $16^\circ$  incidence angle was performed assuming normal incidence and were compared to the results gained under proper consideration of the angle of incidence. The comparison was performed in the following way. We employed the sets of oscillator parameters resulting from the proper DA for the angles of incidence  $8^\circ$ ,  $16^\circ$  and  $60^\circ$  in order to simulate reflectance spectra for an angle of incidence at  $40^\circ$  again implementing the proper approach. The same procedure, only performing improper DA, i.e. assuming normal incidence, was undertaken for the spectra recorded at  $8^\circ$  and  $16^\circ$ . The simulated  $40^\circ$  incidence angle spectra (based on dielectric function tensors obtained employing proper and improper approaches) were then compared with the experimental spectra and the mean squared differences between experimental and simulated spectra were computed. This approach represents one possible test for the quality of the dielectric tensor function generated by the oscillator parameters (other possibilities are the simulation of the reflectance or scattering spectra of randomly oriented polycrystalline samples). In addition to their use for optical calculations, the oscillator parameters also allow gaining insight into structure-property relationships. Therefore we also investigated the dependence of the individual oscillator parameters on the employment of the normal incidence approximation to assess the justification of its use.

The paper is organized as follows: after details about the experimental conditions are provided, a short overview of the theoretical background is given. In the results section we first present the outcome of the six different dispersion analyses carried out in this work. Then we test the validity of the resulting dielectric tensor functions by simulating reflectance spectra at an angle of incidence of  $40^\circ$ . Afterward we assess the dependence of the individual oscillator parameters on the applied



**Fig. 1.** Experimental conditions under which the spectra from the  $a$ - $c$  crystal face have been recorded.  $a$  and  $c$ : crystallographic axes (the  $b$  axis is oriented along the direction of view);  $\beta$ : crystallographic angle;  $x, y, z$ : internal right-handed orthogonal system fixed inside the crystal ( $y$  along the  $c$ -axis,  $z$  along the  $b$ -axis);  $X, Y, Z$ : external right-handed orthogonal system defined by the polarization direction ( $X$ ) and the plane of incidence ( $YZ$ ).

formalism. The paper closes with the section summary and conclusion.

## 2. Experimental

Single crystals of  $\text{K}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  were obtained by a slow evaporation of an equimolar aqueous solution of  $\text{K}_2\text{SO}_4$  and  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ . It crystallizes in the  $P2_1/a$  space group with  $Z=2$  and parameters of the unit cell:  $a=898.5(3)$ ,  $b=1216.7(6)$ ,  $c=612.8(2)$  pm;  $\beta=105.08(2)$  [25]. The orientation of the  $b$ -axis was determined by employing polarized IR radiation following a procedure explained in [18]. The orientations of the  $a$ - and the  $c$ -axis were obtained by an optical goniometer using additionally morphological information. Subsequently, the crystal was polished in a way that a surface with optical quality parallel to the crystallographic  $a$ - $c$ -plane was obtained.  $s$ -polarized spectra (polarization vector perpendicular to the plane of incidence) were recorded from these planes as presented in Fig. 1. In this figure the dependence between the crystallographic axes, the internal coordinate system  $x, y, z$ , the polarization direction  $X$  and the direction of rotation of the crystal is detailed (to obtain spectra for different polarization directions the crystal was rotated to preserve  $s$ -polarization). The radiation impinges under an angle  $\alpha$  (the angle of incidence) in the  $Y$ - $Z$  plane and is polarized along the  $X$ -axis (the  $Z$ - and the  $z$ -axis are oriented along the direction of view and coincide with the crystallographic  $b$ -axis). Here we would like to point out that this arrangement is the same as the one in [8], and differs from the one in our mutual work [18].

The  $s$ -polarized IR spectra were recorded on a Varian 3100 FT-IR spectrometer using a Seagull reflectance cell for incidence angle of  $8^\circ$ ,  $16^\circ$ ,  $40^\circ$  and  $60^\circ$ , employing an Al/KRS5 polarizer. Each spectrum was recorded at  $4 \text{ cm}^{-1}$  resolution using 128 interferogram scans and strong apodization, resulting in spectrum files containing data points at every  $2 \text{ cm}^{-1}$ . Interpolation was performed on each recorded spectrum before the process of fitting, so that the fitted reflectance spectra had reflectance data for each  $\text{cm}^{-1}$ . This was done in order to improve the fitting procedure. The number of parameters fitted was 91 (88 vibrational parameters for the 22 bands, plus the 3 values for the high frequency dielectric tensor). On the other hand, the number of fitted points was 22,004 (5501 points for each of the four spectra recorded at different polarization angle but fitted at the same time). The fitting of the reflectance spectra recorded from the  $a$ - $c$  crystallographic plane carried out employing in parallel four reflectance spectra, recorded at  $\phi=0^\circ, 45^\circ, 90^\circ$  and  $135^\circ$  (cf. Fig. 1) was performed using programs developed by the authors, based on the Mathematica program package.

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