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# COMPOSITION DETERMINATION OF SOME $A^{II}B^{VI}$ TERNARY SEMICONDUCTORS FROM QUASI-FORBIDDEN REFLECTION INTENSITY

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The aim of the present paper is to study the possibility of application of the X-ray quasi-forbidden reflection method to the composition determination of the sphalerite-type  $Cd_{1-x}M_xTe$  ( $M = Mg, Zn, Mn$ ) single crystals. The method is based on the property of quasi-forbidden reflections that their integral intensity is very sensitive to composition and weakly sensitive to crystal lattice defects. An example of application for a  $Cd_{1-x}Mn_xTe$  single crystal is presented.

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## 1. Introduction

The X-ray quasi-forbidden reflections ("XFR") method (proposed in Refs. [1, 2]) is based on determination of the ratio of quasi-forbidden (QF) reflection intensities for the investigated crystal and for a reference binary crystal. This method has been previously used in diffraction studies of the homogeneity of  $A^{III}B^V$  single crystals [2], determination of deviation from stoichiometry in semiconductors [1-3] and transition metal carbides [4] and has been also applied to analysis of site occupation of some dopant atoms in semiconductor crystals [2]. An application of the XFR method for composition studies of  $Ga_{1-x}Al_xAs$  [2, 5] pseudobinary compounds has been reported. In the present paper we discuss the influence of composition of  $Cd_{1-x}M_xTe$  single crystals on the intensity of QF reflections.

## 2. Principle of the method

The diffracted X-ray intensity depends on the structure factor,  $F$ . Let us consider an AB compound of sphalerite type (space group  $F\bar{4}3m$ ). For reflections where the Miller indices satisfy the relation

$$h + k + l = 4n + 2, \quad (n = 0, 1, \dots), \quad (1)$$

the structure factor is

$$F = 4(f_A - f_B). \quad (2)$$

Its value becomes extremely low if the values of the atomic scattering factors,  $f_A$  and  $f_B$ , are very close to each other. Equation (2) is an ideal formula assuming that A and B sites are fully occupied by respective atoms. For ternary  $\text{Cd}_{1-x}\text{M}_x\text{Te}$  compounds the expression (2) becomes

$$F = 4[(1-x)f_{\text{Cd}} + xf_{\text{M}} - f_{\text{Te}}]. \quad (3)$$

It is clear from Eq. (3) that the QF reflections are sensitive to the  $x$  value. On the other hand they are not very sensitive to crystal defects because their intensity may be satisfactorily described by the kinematic theory of X-ray diffraction [1, 3]. In this approach the intensities are proportional to  $|F^2|$ , and the intensity of the beam diffracted by a perfect crystal,  $I_{\text{perfect}}$ , is equal to that of the mosaic one,  $I_{\text{mosaic}}$ :

$$I_{\text{perfect}} = I_{\text{mosaic}}. \quad (4)$$

The ratio of the experimental integrated intensity for CdTe,  $I_0$ , and that for the solid solution,  $I_x$ , determines the  $x$  value [5, 6].

### 3. Results and discussion

The intensity ratio was calculated for Cu  $K_\alpha$  radiation with the following formula [5]:

$$\frac{I(x)}{I(0)} = \frac{|F(x)|^2 \mu(0) \sin 2\theta_0 (1 + \cos^2 2\theta)}{|F(0)|^2 \mu(x) \sin 2\theta (1 + \cos^2 2\theta)}, \quad (5)$$

where  $I(0)$  and  $I(x)$  denote the measured integrated intensity of the QF reflection for the binary and ternary compound, respectively,  $\mu(x)$  is the linear absorption coefficient of the ternary compound,  $\theta_0$  and  $\theta$  are the Bragg angles for the QF reflection of the binary and ternary compound, respectively. The intensity ratio is shown in Figs. 1a-3a. Figures 1b-3b show the ratio  $I_{\text{perfect}}/I_{\text{mosaic}}$  computed for some reflections as a function of  $x$ . For Cu radiation Eq. (4) is satisfied in a large  $x$  range for high-angle QF reflections (e.g. 600) and in a small  $x$  range for low-angle QF reflections (e.g. 200). For the Mo radiation the range of  $x$ , where Eq. (4) is satisfied, is considerably smaller for all QF reflections. Therefore we have chosen for the analysis the Cu radiation. The curves for allowed (strong) reflections 111, 333 in Figs. 1a-3a illustrate the fact that allowed reflections are not suitable for precise composition determination due to the weak intensity dependence on  $x$ . Their intensity may be considerably influenced by the defect structure (as 111, see Figs. 1b-3b).

The integrated intensities were determined for experimentally obtained rocking curves of 200 and 600 QF reflections for (100) oriented CdTe and  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  single crystals. The rocking curves of these reflections were collected using a high-resolution diffractometer equipped with a Bartels-type monochromator yielding parallel Cu  $K_{\alpha_1}$  beam. Measurements of the lattice constants were performed by the powder method to determine the Mn content from the linear dependence (Vegard's rule) [7]:

$$a = 6.480 - 0.151x. \quad (6)$$

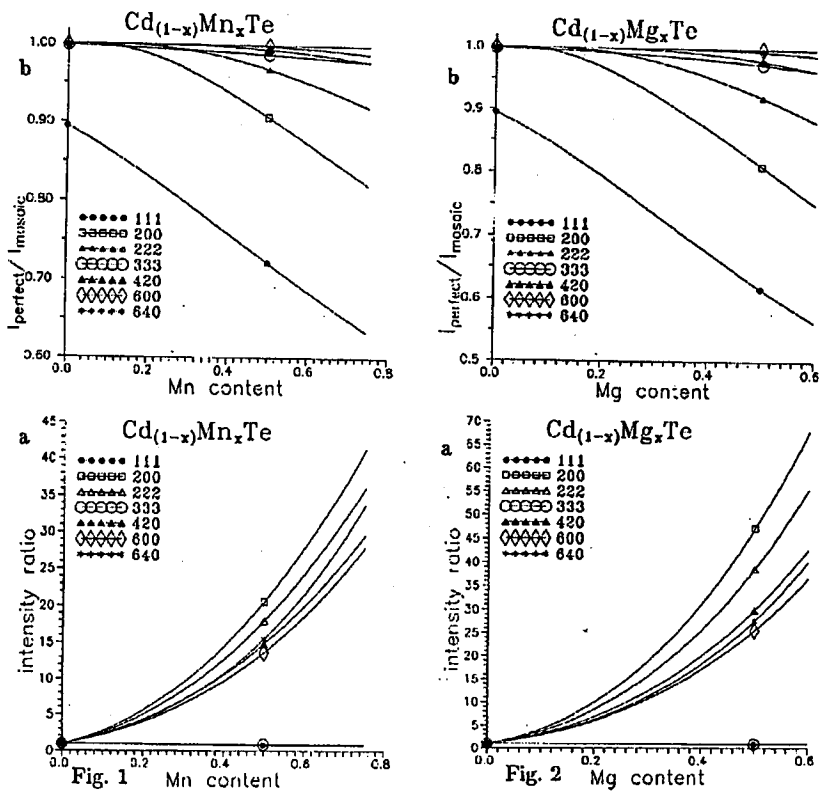


Fig. 1. Intensity ratio (a) and  $I_{\text{perfect}}/I_{\text{inosaic}}$  (b) for  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  as a function of  $x$  for selected allowed and QF reflections. The calculations were performed for the  $\text{Cu } K_{\alpha_1}$  wavelength.

Fig. 2. The same as in Fig. 1 but for  $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ .

The measurements were carried out using various vertical and horizontal slits on the incident beam (from 0.5 to 2 mm) to enable X-ray illumination of various areas of the samples. The intensity ratios were virtually the same for all applied slits. For the 200 reflection of a  $\text{Cd}_{0.50}\text{Mn}_{0.50}\text{Te}$  crystal (nominal composition) the method gives  $x = 0.460$  differing marginally from  $x = 0.457$  calculated from Vegard's rule. For the 600 reflection the obtained  $x$  value is underestimated ( $x = 0.220$ ). A similar discrepancy for the 600 QF reflection has been observed for  $\text{GaAs:In}$  crystals; it has been explained by the influence of the atomic displacement of As neighbours of In atoms on intensity (this effect is stronger for the 600 reflection than for 200) [2].

The combination of the QFR method with the Bond method creates a possibility to investigate the dependence of the lattice parameter on composition with the rarely satisfied condition that values of  $a$  and  $x$  are measured for the same crystal volume. This is important especially for ternary  $A^{II}B^{VI}$  compounds for which composition inhomogeneities are often observed.

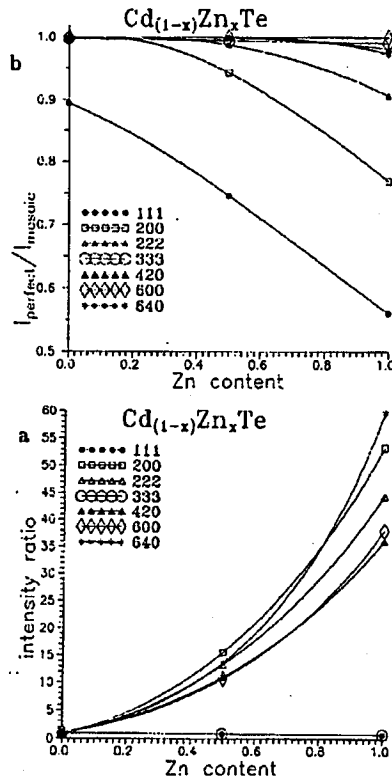


Fig. 3. Intensity ratio (a) and  $I_{\text{perfect}}/I_{\text{mosaic}}$  (b) for  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  as a function of  $x$  for selected allowed and QF reflections. The calculations were performed for the  $\text{Cu } K_{\alpha_1}$  wavelength.

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