Distribution of Electrons in Cadmium Sulfide Crystals*

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Very accurate x-ray diffraction intensities from a "pure" CdS crystal and one doped with chlorine were used to calculate electron density maps of their crystal structures projected along the c axis. To eliminate series termination errors, a difference map obtained by subtracting the electron density of the "pure" crystal from that of the doped crystal was also prepared. According to this map, the electron distribution in the doped crystal is smeared out in the vicinity of the atom centers and an excess of electrons occurs in interstitial sites. This is contrary to the recently reported findings of Shuvalov who observed the formation of "electron bridges" along lines joining adjacent atoms. It is concluded that our observations are consistent with a partial disorder introduced in the doped crystal by the substitution of chlorine into sites normally occupied by sulfur atoms. Observed variations between corresponding x-ray intensities of the doped and undoped crystal can be similarly explained by changes in the extinction effect due to this disorder.

R ECENTLY Shuvalov[1,2] reported observing differences in the electron distributions of cadmium sulfide crystals whose dark resistivities ranged from 2.5 to 10^5 ohm-cm. Specifically, he shows electron density projections on (0001) of two crystals representative of extremes in this range. The projection of the high-resistivity crystal consists of strong maxima in positions where the cadmium and sulfur atoms overlap and a more or less random background elsewhere, whereas that of the low-resistivity crystal shows a marked increase in the electron density along lines joining adjacent atom positions (Fig. 1). Shuvalov attributes the increase in conductivity to the formation of these "electron bridges." Next, he correlates the changes in the electron distribution to measured differences of certain sets of x-ray diffraction intensities and, although the correlation in his own words is not too precise, reports that corresponding changes in similar intensities occur
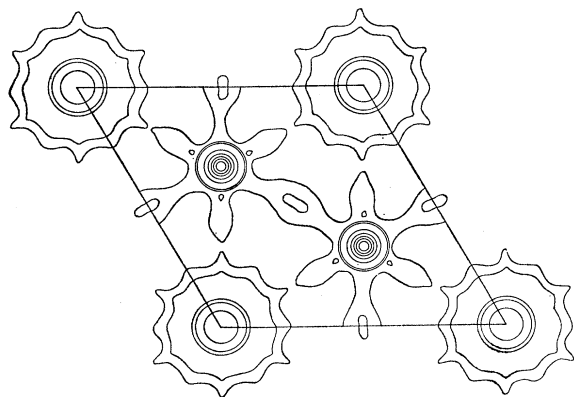

FIG. 1. Electron density of a high-conductivity CdS crystal projected on (0001) by Shuvalov.[1] The contours at the corners of the unit cell surround slight depressions rather than peaks.

when the conductivity in CdS crystals is increased either thermally or by exposure to visible light. Similar correlations between such intensities of x-ray reflections and electrical conductivity were also observed by Aigler[3] who observed a decrease in the conductivity of CdS crystals when they were placed in a magnetic field parallel to their c axes. The above results are based on x-ray diffraction intensities measured by photometering $hk0$ reflections on Weissenberg photographs. Because of the obvious importance of the above findings to the understanding of photoconductive processes in CdS, it was decided to redetermine the electron distributions in our laboratory using more accurate x-ray data.

Two needle-shaped crystals about 75 microns in diameter were chosen for this investigation. One was a relatively "pure" crystal having a dark resistivity of 10^{12} ohm-cm and the other was a chlorine-doped crystal whose dark resistivity was 10^2 ohm-cm. A Buerger single-crystal diffractometer[4] equipped with a scintillation counter was used to measure the intensities of all $hk0$ reflections out to $\sin\theta/\lambda = 1.20$ using Ag $K\alpha$ x radiation. The measured intensities were corrected for absorption, Lorentz-polarization, anamolous scattering, and extinction effects. Sets of symmetry-related reflections were used to measure each reflection independently at least twice and the internal agreement of all the intensities was better than 2%. After converting the intensities to structure factors on an absolute scale by the Wilson method,[5] electron density projections on (0001) were computed for each crystal using an IBM 704 calculator. Despite the relatively large number of amplitudes used (more than twice the number employed by Shuvalov), the electron densities appeared to contain ripples in the vicinity of the main peaks due to series termination effects. These effects were eliminated, therefore, by calculating a "difference" synthesis by subtracting the electron density of the undoped crystal

[1] Yu. N. Shuvalov, Doklady Akad. Nauk (U.S.S.R.) 109, 753 (1956) [translation: Soviet Phys.—Doklady 1, 490 (1957)].

[2] Yu. N. Shuvalov, Zhur. Tek. Fiz. (U.S.S.R.) 26, 1870 (1956) [translation: Soviet Phys. (Tech. Phys.) 1, 1809 (1957)].

[3] G. G. Aiger, Zhur. Tek. Fiz. (U.S.S.R.) 28, 1933 (1958) [translation: Soviet Phys. (Tech Phys.) 3, 1776 (1958)].

[4] M. J. Buerger, *Crystal-Structure Analysis* (John Wiley & Sons, Inc., New York, 1960).

[5] A. J. C. Wilson, Nature 150, 152 (1942).

from that of the doped crystal at each point xy in the projection. The resulting map is shown in Fig. 2 which includes three unit cells of the crystal. As can be clearly seen, there are no "electron bridges" present between adjacent atoms. Instead, there appear to be rings of "excess" electron density surrounding the positions of the overlapping Cd and S atoms. These rings are probably due to the larger effective size of the atoms in the doped crystal which, in turn, is caused by the partial disorder produced by the substitution of chlorine atoms into sites normally occupied by sulfur atoms. In addi-
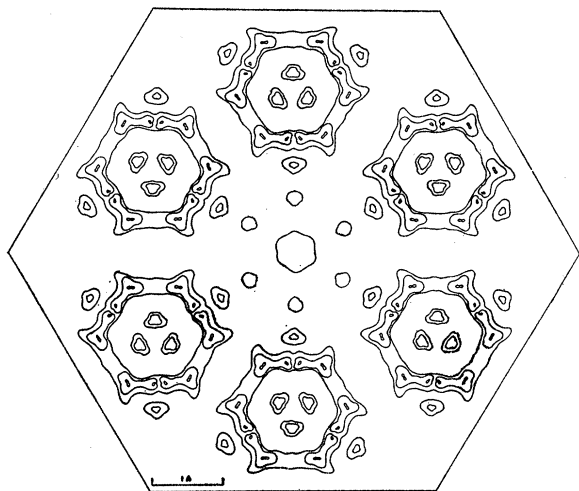

FIG. 2. Difference synthesis obtained by subtracting the (0001) electron density projection of a pure CdS crystal from that of a doped crystal. Positive contours only are shown for clarity.

tion, a relatively low peak is formed at the corners of the unit cell (shown only at the center of Fig. 2) suggesting that a very small fraction of the atoms are displaced to interstitial sites. On the basis of the contour height it is estimated that this peak corresponds to a displacement of one out of a thousand atoms in the crystal.

Because the intensity correlations reported by Shuvalov show trends rather than actual correspondence to differences in conductivity, it is not surprising that our intensity differences fail to agree exactly with those
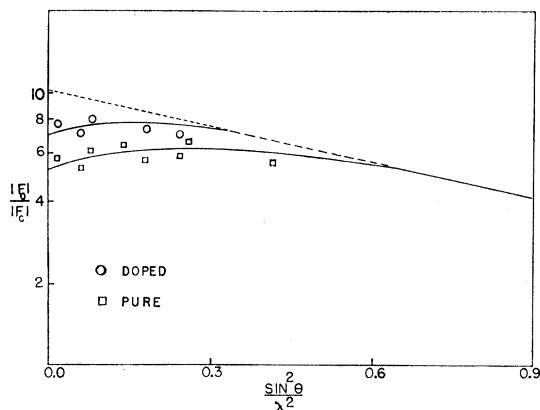

FIG. 3. Curves of $\ln|F_0/F_c| = K - B \sin^2\theta/\lambda^2$ for pure and doped CdS, where F_0 is the observed and F_c the calculated structure factor of a reflection, K is a scaling constant, B is the temperature coefficient, θ is the Bragg angle, λ is the wavelength of the x radiation used.

reported by him. Moreover, we believe that the differences in intensity are markedly affected by extinction effects which are bound to be different in pure and doped crystals. The importance of extinction is shown by the Wilson-type plots[5] in Fig. 3 which compare the ratios of observed and calculated structure factor amplitudes before correcting them for extinction, for the doped and undoped crystal. The larger extinction in the pure crystal is clearly shown by the larger deviation of the measured ratio from the straight line at small Bragg angles. It is concluded, therefore, that "electron bridges" do not form in CdS crystals when their conductivity is increased and that changes in the electron density of doped crystals can be adequately explained in terms of substitutional and interstitial impurities, whereas their intensities are largely altered by changes in the extinction effects.

ACKNOWLEDGMENTS