

## LETTERS TO THE EDITOR

*Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the eighteenth of the preceding month, for the second issue, the third of the month. Because of the late closing dates for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.*

**Communications should not in general exceed 600 words in length.**

**Electron Distribution in ZnO Crystals**

In discussing the nature of the binding forces in various crystals one finds cases in which the usual criteria for their classification as electrostatic, homopolar, or polarization forces will not decide the point. We wish to report briefly on the application to ZnO of a method of approach to this problem through the interpretation of x-ray or electron diffraction intensities. A detailed account of this work will appear elsewhere.<sup>1</sup>

Intensities in the electron diffraction pattern from ZnO show<sup>2</sup> large deviations from values computed from the centrally symmetric charge distributions of Pauling and Sherman<sup>3</sup> for the Zn and O atoms. The anomalies are obvious on visual inspection, the order in intensity of quite prominent rings being reversed from that expected. Though x-ray intensities do not show these prominent anomalies, Lark-Horovitz and his co-workers were forced to the conclusion that they are due not to some factor in the experimental methods, but to the nature of the charge distribution in the crystal.

The ZnO crystal is of the hexagonal close packed type. Each zinc atom lies near the center of a tetrahedron formed by four oxygen neighbors, but nearer by 0.1Å to one of these oxygen atoms than to the others; each pair of zinc-oxygen nearest neighbors lies parallel to the *c* axis. Yearian has noted that one might account qualitatively for the observed intensities by assuming a shift of the *M* shells of the zinc atoms along the *c* axis, toward the nearest oxygen neighbors. However, Johnson and Nordheim<sup>1</sup> have shown that any such polarization which might arise from intracrystalline fields can account for only some 1/160 of the observed effect. We have thus been brought to the conclusion that the valence electrons in the crystal, despite their small numbers, are responsible for the observed anomalies.

Since a more direct test of this idea is not practicable at present, we have sought a simple and qualitatively reasonable model for the charge distribution in the crystal which will give the observed electron diffraction intensities. To the spherically symmetric distributions of Zn<sup>++</sup> and O we have added various linear distributions of the valence electrons, or, with better results, distributions over the surfaces of ellipsoids of revolution. To account for the observed intensities we find it necessary to concentrate the valence electrons in the region between each zinc atom and its nearest oxygen neighbor; distributions which treat the four oxygen neighbors of a zinc atom as equivalent cannot give the desired results. Good agreement with Yearian's observations is given by a distribution of three

("valence") electrons over ellipsoids which enclose each pair of zinc-oxygen nearest neighbors. The major axis of the ellipsoids is 2.1Å in length, the minor axis 0.35Å. The greater part of the charge must be placed on the half of the ellipsoid nearer the zinc.

This model gives satisfactory agreement with observation for all strong lines, in particular accounting correctly for their order in intensity. Minor discrepancies remain, and the agreement is quite poor for the weak lines with the Miller index *l*=4. The accuracy of the experimental results does not justify a more elaborate attempt to reconstruct the charge distribution. However, we believe that the agreement obtained indicates conclusively that the actual electron distribution involves a concentration of valence electrons in the region between the zinc-oxygen nearest neighbors or a marked unidirectional distortion of the distribution of outer electrons in the zinc, such as is known to exist in those diatomic gases which can be treated theoretically.

K. Lark-Horovitz and C. H. Ehrhardt<sup>4</sup> have obtained further verification of this conclusion by carefully measuring x-ray diffraction intensities, from which they can deduce the corresponding electron intensities. Their observations show general agreement with the observed electron intensities, and particularly satisfactory agreement with intensities computed from a model like that described above, but with two electrons distributed over the ellipsoid instead of three.

The charge distribution thus found seems to indicate that in the crystal ZnO molecules tend to maintain their individuality, in contrast to the situation in purely ionic crystals. It suggests also that the homopolar binding of ZnO nearest neighbors is responsible in this crystal for the departure from the complete tetrahedral symmetry such as diamond exhibits. The ZnO pairs will of course not form an electrically symmetrical complex, and the binding of the molecules into the crystal will involve electrostatic and polarization forces, and probably some contribution from homopolar binding as well.

We are indebted to Drs. K. Lark-Horovitz and H. J. Yearian for many helpful discussions of this problem.

HUBERT M. JAMES  
VIVIAN A. JOHNSON

Purdue University,  
Lafayette, Indiana,  
June 1, 1939.

<sup>1</sup> Johnson, *Zeits. f. Krist.*, to appear soon.

<sup>2</sup> H. J. Yearian and K. Lark-Horovitz, *Phys. Rev.* **42**, 905 (1932).  
K. Lark-Horovitz, H. J. Yearian and J. D. Howe, *Phys. Rev.* **47**, 331 (1935). H. J. Yearian, *Phys. Rev.* **48**, 631 (1936).

<sup>3</sup> L. Pauling and J. Sherman, *Zeits. f. Krist.* **81**, 1 (1932).

<sup>4</sup> K. Lark-Horovitz and C. H. Ehrhardt, *Phys. Rev.* **55**, 605 (1939).