

A NOTE ON VOLUME RECTIFICATION OF CRYSTALS

By S. R. KHASTGIR

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Recently a paper has been published on volume rectification by B. K. Sen (1942). The paper appears to be an elaboration of what was reported by the same author (1937) about five years ago. Deaglio (1938) at that time, in a note published in *Nature*, made a clear statement about volume rectification which is only a natural consequence of the lack of symmetry in *polar* crystals. He also referred to the experimental evidence of such volume rectification in his experiments with carborundum and made the present position with regard to the rectifying properties of crystals abundantly clear. Yet it has been concluded by Sen in his recent paper that "the volume rectification effect is not confined to crystals like carborundum, zincite and silicon alone, which have no centres of symmetry but that it is also exhibited by crystals like galena, iron-pyrites and pyrolusite, possessing centres of symmetry." In view of such conclusion, a brief review of the subject is given here to leave no room for any misunderstanding about the existence of volume rectification in *polar* crystals.

My experiments with Das-Gupta (Khastgir, 1935) showed that when carborundum, zincite or silicon crystal was placed between two mercury electrodes giving large contact areas, there was considerable rectification. Similar experiments with symmetrical crystals like iron-pyrites, galena, etc., showed no rectification. The carborundum crystal under examination exhibited one plane face and other facets and it consisted of at least two crystals twinned together. Of the symmetrical crystals, the iron-pyrites and magnetite crystals used in these experiments could be regarded as single crystals. The results of these experiments strongly *suggested* asymmetric conductance in crystals having no centres of symmetry. The fact that the rectification observed in carborundum, zincite and silicon crystals did not change, when one of the crystal surfaces was heated, seemed also to support this suggestion. As there was no experimental test that the surface effect was entirely eliminated in our experiments, the evidence of volume rectification in polar crystals was not regarded as conclusive. Crucial tests were therefore considered necessary. Such a crucial test was made a few months later by Deaglio (1935) who performed two sets of experiments. In the first set of experiments, the plane natural face of the carborundum crystal which was perpendicular to the axis of six-fold symmetry and the face opposite to it, scraped and made plane, were coated with gold or platinum by cathodic sputtering. The I-V characteristic curve obtained with

such crystal between two electrodes making large contact areas showed considerable rectification. No electrolytic polarisation was observed but there was photo-electric effect on the crystal surface. The observed rectification was considered as *mainly* due to rectification of the "barrier layer"-type. In the second set of experiments, both the faces of a carborundum single crystal were scraped and made smooth. The electrodes were gold or platinum films deposited on the scraped surfaces. There was no trace of any electrolytic polarisation and there was also no evidence of any Dember effect or any internal photo-electric effect. The characteristic curves were then drawn for two different thicknesses of the same crystal keeping the contact-areas the same. The rectification observed was opposite in sign to that observed in the first set of experiments. When curves were drawn showing *current* against *voltage per cm.* for the two different thicknesses of the crystal, they were found to be almost identical. This showed that the observed rectification was not due to any surface effect. There was thus no room for any doubt as to the existence of volume rectification, at least in carborundum crystals.

This asymmetric conductivity was studied later in the experiments of Khastgir and Chakravarty (1937) when the potential fall in the body of the carborundum crystal was observed for an applied voltage sending current in the two opposite directions. With carborundum, the potential distribution was found to be different for the two opposite directions. In the single crystals of iron-pyrites and magnetite, however, the potential distribution remained exactly the same for the two opposite directions of the current.

It is likely that Tissot (1910) and Pierce (1912) also detected volume rectification years ago in some crystals. They showed that with a certain group of crystals, even relatively large polished plates between metallic electrodes made very sensitive detectors. It is evident that the rectification observed by them in the symmetrical crystals was a *surface* effect; whereas, in the crystals with no centres of symmetry, the effect must have been a combination of *surface* and *volume* rectification.

On the theoretical side, R. de L. Kronig (1926) showed in a general way that the crystal rectification could be due to asymmetric binding of the ions into positions of equilibrium by restoring forces, not symmetrical for equal and opposite displacements. Considering the isothermal variation of the electrical resistance with the applied voltage (which was called "electro-resistive" effect), Osterberg (1936) also gave a theoretical treatment of rectification in carborundum crystals. The resistance was shown theoretically to change, on reversing the sign of the applied voltage by an amount depending upon the electro-resistive constants of the crystal. Carborundum crystals were actually found to rectify current in the manner predicted along the direction of the axis of six-fold symmetry.

In conclusion, it can be said that Sen's observations of the rectification effect in symmetrical crystals like galena, iron-pyrites, pyrolusite, etc., placed

between mercury electrodes of large contact areas, merely showed that the surface effects were not eliminated in his experiments.

PHYSICS DEPARTMENT,
DACCA UNIVERSITY

R E F E R E N C E S

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