

equal, that modulation should be in phase at conjugate points. The observed periodicities also accord reasonably with Dungey's⁵ treatment of hydromagnetic oscillations in the exosphere. From this we should expect the periods of 2.5–8.5 min observed at Kiruna to be scaled up by a factor of about 2.6 at Great Whale River and Byrd. The observed periodicities, 3–16 min, are indeed longer than those at Kiruna, though perhaps not quite as long as expected. On the other hand, our observation does not in itself prove that hydromagnetic waves are the cause of the fluctuations. It only limits the choice to mechanisms acting symmetrically with respect to the equatorial plane.

It is interesting to note that these absorption fluctuations, which are in phase at conjugate points, occur in just that part of the day when the slow fluctuations, which have periods up to 2 h and are in antiphase at conjugate points⁶, are least common. This might mean that different parts of the exosphere tend towards different modes of oscillation. However, further phenomena will no doubt come to light before the picture is complete.

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¹ Brown, R. R., *J. Geophys. Res.*, **69**, 2315 (1964).

² Hartz, T. E., Montbriand, L. E., and Vogan, E. L., *Canad. J. Phys.*, **41**, 581 (1963).

³ Sugiura, M., *J. Geophys. Res.*, **66**, 4087 (1961).

⁴ Nagata, T., Kokubun, S., and Iijima, T., *J. Geophys. Res.*, **68**, 4621 (1963).

⁵ Dungey, J. W., *Geophysics*, edit. by Dewitt, Hieblot and Lebeau, 540 (Gordon and Breach, 1963).

⁶ Chivers, H. J. A., and Hargreaves, J. K., *Nature*, **202**, 891 (1964).

PHYSICS

Metastability of Amorphous Structures

In earlier papers^{1–4} we developed a free-volume model for the amorphous phase according to which the liquid and glassy states of a given substance together comprise a single, thermodynamically well-defined phase. In this model the transition to the glass state results ideally from the freezing out of the free volume, and hence the configurational entropy of the liquid⁵. This transition should occur in all classical liquids, including monatomic ones, provided crystallization is by-passed². Implicit in these ideas is the hypothesis that the glassy state is truly metastable and not unstable; consequently, by the Nernst theorem, it would have vanishing entropy at 0° K. For the hypothesis to be true, each microscopic structural unit of the glass must lie at a position of static equilibrium, the totality of which is randomly distributed. If one such structure exists there must be a large number of similar random structures of equal energy. Nevertheless, the entropy of each is zero, because all these structures are mutually inaccessible. One particular structure would be picked out in a given cooling process, and the system would remain in that structure. The increase of entropy on heating back into the liquid state would then occur because the equivalent random structures become mutually accessible⁵.

This hypothesis of metastability is supported by some recent observations on model systems and by recent computations of Rahman.

It had been found⁶ that a random arrangement of hard spheres will compress to a rigid and apparently amorphous structure (dense random structure) with a unique density (0.86 times that of ideal close packing). The detailed

observations of nearest neighbour contacts in this structure carried out by Bernal *et al.*⁷ indicate that each sphere is rigidly locked into position within a truly amorphous structure. It follows that the Bernal dense random structure satisfies the condition of mutual inaccessibility of equivalent structures and hence is metastable; it therefore constitutes the prototype of the monatomic glass predicted in our earlier papers. Stillinger, DiMarzio and Kornegay⁸ have shown that a random two-dimensional assembly of uniform hard disks also collapses to a rigid dense random structure which they consider to be a model for a two-dimensional glass.

Recently, Rahman⁹ carried out machine calculations of the trajectories of a collection of 864 spherical atoms interacting via a 6–12 potential appropriate to argon and held at a density equivalent to that of crystalline argon at 40° K and one atmosphere pressure. Under the conditions of his calculations, he finds that the liquid state of this system can be 'quenched' in a period of 10⁻¹² sec to a temperature of 10° K without crystallization. In effect, these calculations of Rahman may be regarded as equivalent to a laboratory experiment in which minute droplets of liquid argon are quenched rapidly. They further confirm the high resistance of amorphous systems, even when monatomic, to the initiation of crystallization.

Inasmuch as the hypothesis of metastability is intuitively most difficult to accept for monatomic systems, we regard these two instances of its correctness as convincing evidence for its general validity.

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¹ Turnbull, D., and Cohen, M. H., *J. Chem. Phys.*, **29**, 1049 (1958).

² Cohen, M. H., and Turnbull, D., *J. Chem. Phys.*, **31**, 1164 (1959).

³ Turnbull, D., and Cohen, M. H., *J. Chem. Phys.*, **34**, 120 (1961).

⁴ Turnbull, D., and Cohen, M. H., in *Modern Aspects of the Vitreous State*, edit. by MacKenzie, J. D., **1**, 38 (1960).

⁵ These results are analogous to those obtained by Gibbs and DiMarzio (*J. Chem. Phys.*, **28**, 373; 1958) with a lattice model specifically applicable to molecularly complex systems.

⁶ (a) Rice, O. K., *J. Chem. Phys.*, **12**, 1 (1944). (b) Scott, G. D., *Nature*, **188**, 908 (1960). (c) Bernal, J. D., and Mason, J., *Nature*, **188**, 910 (1960).

⁷ Bernal, J. D., *Nature*, **183**, 141 (1959); **185**, 68 (1960). Also see ref. 6(c).

⁸ Stillinger, F. H., DiMarzio, E. A., and Kornegay, R. L., *J. Chem. Phys.*, **40**, 1564 (1964).

⁹ Rahman, A., Argonne National Laboratory (private communication).

Electrical Conduction in Amorphous Films

WHILE carrying out general exploratory work on the electrical properties of vacuum-deposited thin films, an interesting phenomenon was observed in boron layers. Similar effects have since been observed in other materials; however, most of the work so far has been with boron films. The purpose of this communication is to describe the observed phenomenon, leaving the explanation to a later date when more facts have been collected.

The boron layers were deposited by direct electron bombardment in a vacuum of about 10⁻⁶ mm mercury. An electron beam was focused on an extremely pure boron rod which rested on a carbon pedestal. Every precaution was taken to bombard only the boron and not the pedestal. The carbon pedestal was of spectroscopic grade purity. A beam current of approximately 120 m.amp at a voltage of about 10 kV was found sufficient to obtain a deposition rate of 100–200 Å/min.