

cuit, and  $f_p$  is measured using a marginal oscillator and frequency counter. The change in  $f_p$  with pressure reflects change in the product  $LC$ . Now, the change in the inductance of the coil can be measured accurately in a separate experiment using the coil technique for compressibility measurement mentioned earlier. This also determines the compressibility. The change in capacitance of the condenser reflects a dimensional change and change in the dielectric constant of the sample. This follows from the relationship for the capacitance of a parallel plate condenser; namely

$$C = \epsilon_0 \epsilon \frac{A}{d} \quad (8)$$

where  $\epsilon_0$  is the permittivity of free space,  $\epsilon$  is the dielectric constant of the sample,  $A$  is the surface or plate area of the condenser, and  $d$  is the plate separation. The effect of the dimensional change on  $C$  can be calculated from the known compressibility. Fortunately, this effect turns out to be much smaller than the change due to  $\epsilon$ , even for low dielectric constant materials (21,22). Thus we see that the various effects can be separated out and the dielectric constant determined.

#### MEASUREMENT OF IONIC CONDUCTIVITY IN SOLIDS

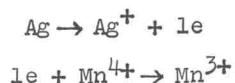
Two methods have been used generally for studying ionic conductivity in solids. The first is the conductance method. Sample conductance is measured with an impedance bridge. Alternating current is used to eliminate electrode-polarization effects. The second method is the tracer-diffusion method. Here a long period of time is generally needed for the tracer to diffuse an appreciable distance through the solid. Data on ionic mobilities and diffusion coefficients are obtained by sectioning and analyzing the sample.

A novel approach for possible use in the study of ionic conductivity under pressure is that of the recently developed solid electrolyte ionic cell (26). The cell consists of a sequential layering of the following components: A metal anode, a metal halide, an oxidizing agent, and a cathode.

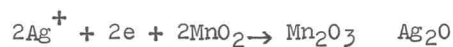
One example is



where Ag is the anode and AgI is the ionic conductor. Cells such as this produce voltages of the order of 400-600 millivolts. The electrochemical reaction can be described as



and the overall reaction:



In low-resistance circuits, current flow in such cells is inefficient and nonlinear. However, in high resistance (essentially open) circuits, they perform quite satisfactorily with cell voltage remaining constant for a long period of time.

A typical response curve of voltage versus pressure at room temperature is shown in Fig.17. The peak below 5 kbars is associated with the phase transformation in AgI. In the high-pressure phase, the voltage drops nearly exponentially with pressure and is practically zero by about 70 kbars. This behavior is reversible. At higher temperatures, at least up to 400 C, the response is merely displaced to higher pressures.

Current flow is believed to be by diffusion of the charge carriers ( $\text{Ag}^+$  ions in the present case) through the ionic conductor by a defect mechanism. High pressure thus appears to stabilize the structure of the ionic conductor to restrict the diffusion of the carriers. Such behavior is consistent with the conduction mechanism proposed by Kurnick (27) as a result of his studies on AgBr using the conductance method.

The pressure response of cells using AgCl and AgBr has been found to be quite similar to that in Fig.17 except that the absolute value of the

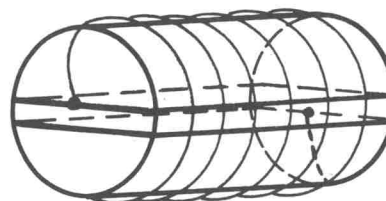


Fig.17 Typical response for the ionic cell at 25 C. The cell assembly is as indicated

voltages are different. By doping the ionic conductor with selected impurities, for example with a salt whose cation or anion is of a different valence, and studying the response of the cell as a function of pressure and temperature, it appears possible, at least in principle, to obtain information about the mobilities of vacancies and interstitials as well as the activation volumes of both Frenkel and Schottky defects.

#### ACKNOWLEDGMENTS

The authors thank Drs. E.H. Poindexter and J.D. Barnett for their many helpful comments, Mr. Frank Becker for his excellent support in component fabrication and Mr. George Tomes for his assistance in performing many of the experiments.

#### REFERENCES

1. G. A. Samara, A. Henius and A. A. Giardini, ASME Publication No. 63-WA-341, 1963 and ASME trans. (in press).
2. P. W. Montgomery, H. D. Stromberg, G. H. Jura, and G. Jura, in High Pressure Measurement, edited by A. A. Giardini and E. C. Lloyd, Butterworths, Washington, D. C. (1963) p.1.
3. G. A. Samara and A. A. Giardini, Rev. Sci. Inst., 35, 989, (1964).
4. P. J. A. Fuller and J. H. Price, Nature 193, 262 (1962).
5. P. W. Bridgman, Proc. Am. Acad. Arts and Sci. 74, 425 (1942).
6. F. R. Boyd and J. L. England, J. Geophys. Res. 65, 741 (1960).
7. G. C. Kennedy and P. N. LaMori, in Progress in Very High Pressure Research, F. P. Bundy, W. R. Hibbard, Jr., and H. M. Strong eds., p. 304, Wiley, New York, 1961. Also see Ref. 14.
8. J. E. Tydings and A. A. Giardini, in High Pressure Measurement, p. 200, op. cit.
9. W. Klement, Jr., A. Jayaraman, and G. C. Kennedy, Phys. Rev. 131, 632 (1963).
10. A. A. Giardini, E. H. Poindexter and G. A. Samara, ASME Publication No. 63-WA-342, (1963) and ASME Trans. (in press).
11. P. T. Hobson and W. P. Osmond, Nature 161, 562 (1948).
12. H. M. Strong, ASME Publication No. , (1964).
13. P. W. Bridgman, Proc. Amer. Acad. Arts and Sci., 74, 21 (1940); 74, 425 (1942); Phys. Rev. 48, 893 (1935).
14. P. N. LaMori, in High Pressure Measurement, p. 321, op. cit.
15. F. E. Terman, Radio Engineers' Handbook, McGraw-Hill, New York (1943), p.98.
16. G. A. Samara, "Effect of hydrostatic pressure up to 25 kbars on the magnetization of Fe, Ni, Co and Fe-Ni alloys" (to be published).
17. L. Patrick, Phys. Rev. 93, 384 (1954).
18. R. M. Bozorth, Ferromagnetism, D. Van Nostrand Co., New York (1951), p.843.
19. F. D. Stacey, Canad. J. Phys. 34, 304 (1956).
20. D. Gagan, Proc. Phys. Soc. 72, 1013 (1958).
21. S. Mayburg, Phys. Rev. 79, 375 (1950).
22. A. J. Bosman and E. E. Havinga, Phys. Rev. 129, 1593 (1963).
23. F. Jona and G. Shirane, Ferroelectric Crystals, The Macmillan Co., New York (1962) pp.41, 142, 290.
24. G. A. Samara, J. Phys. Chem. Solids (in press).