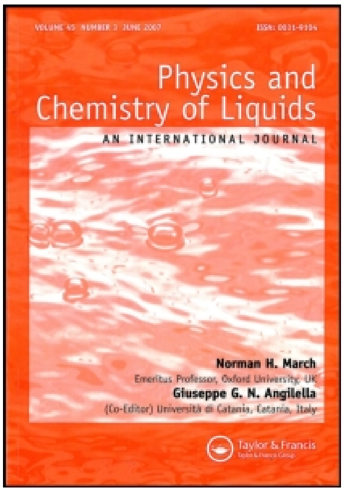

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

The electrical resistivity of liquid indium, tin and lead

H. A. Davies[a][b]; J. S. Llewelyn Leach[b][c]
[a] Department of Metallurgy, University of Sheffield, Sheffield [b] Department of Metallurgy, Imperial College of Science and Technology, London, S.W. [c] Department of Metallurgy, University of Nottingham, Nottingham

To cite this Article Davies, H. A. and Leach, J. S. Llewelyn(1970) 'The electrical resistivity of liquid indium, tin and lead', Physics and Chemistry of Liquids, 2: 1, 1 — 12
To link to this Article: DOI: 10.1080/00319107008084072
URL: http://dx.doi.org/10.1080/00319107008084072

Physics and Chemistry of Liquids. 1970. Vol. 2, pp. 1–12
Copyright © 1970 Gordon and Breach Science Publishers
Printed in Great Britain

The Electrical Resistivity of Liquid Indium, Tin and Lead

H. A. DAVIES‡ and J. S. LLEWELYN LEACH§

Department of Metallurgy
Imperial College of Science and Technology
London, S.W.7

Received October 6, 1969

Abstract—The electrical resistivities of liquid indium, tin and lead have been measured as functions of temperature up to 200–300 °C above their melting points, with an accuracy of ±0.15%. The resistivity of liquid indium was found to be a linear function of temperature but abrupt changes in the temperature coefficient of resistivity were observed for liquid tin and lead. The temperature at which the discontinuity in slope occurred and the absolute resistivity were found to be dependent on purity for liquid tin, but, within the limits of accuracy of the measurement, independent of purity for liquid lead.

Introduction

Prior to the study of the electrical resistivities of the liquid alloy systems indium-lead and indium-tin[1] and gold-tin[2] the resistivities of some of the pure liquid components, namely indium, tin and lead were measured as functions of temperature. Wide variations exist in the published resistivity data for these metals, particularly for tin and indium, and also the resistivity of liquid tin appears to be especially dependent on the purity of the sample.[3] Moreover, large and abrupt changes in the temperature coefficient of resistivity have been reported by one group of workers[4,5] for liquid tin, gallium and bismuth, whereas they did not report such an effect for liquid indium. These changes in the temperature coefficient were thought to be associated with changes in the structure of the liquids and, in the case of tin and gallium, the results of diffraction experiments and other physical property measurements[6,15] give some support to this suggestion. How-

---

‡Present address: Department of Metallurgy, University of Sheffield, Sheffield.

§ Present address: Department of Metallurgy, University of Nottingham, Nottingham.

ever, they have not been confirmed by subsequent resistivity measurements.

This work was intended, therefore, to obtain precise resistivity data for the three liquid metals, to check for possible changes in temperature coefficient and to investigate the dependence of resistivity on sample purity.

Experimental

The resistivities were measured very precisely using a capillary and d.c. four point probe technique, described previously.[2,7] Small bore borosilicate glass capillaries of 0.5 mm. i.d. were used which produced liquid metal threads having a resistance of about 1 ohm. Particular attention was paid to reducing two of the major errors encountered with this technique, arising from the presence of gas bubbles (which often adhere to the capillary wall) and from fluctuations in the environmental temperature.

The capillaries were initially calibrated using triple-distilled mercury at 20 °C and all subsequent measurements were made relative to the resistivity of mercury at 20 °C. The temperature of the environment was stable to better than ± 0.1 °C during a measurement. When these precautions were taken, the random scatter in the data was generally less than ± 0.03% and always less than ± 0.05%. The absolute accuracy of the resistance values is estimated to be better than ± 0.15%.

Results

Indium. The metal, supplied by Johnson Matthey Ltd., was nominally 99.99% pure, the principal impurities being Bi and Pb. Its resistivity (ρ), measured at temperatures between 162 and 400 °C, was a linear function of temperature over the whole range investigated; this is shown in Fig. 1.

The data were fitted to the equation $\rho = A + BT$ $\mu\Omega$ cm, where T is the temperature in °C, by the method of least squares. The calculated values of the constants A and B were: $A = 28.43$ $\mu\Omega$ cm, $B = 2.48 \times 10^{-8}$ Ω cm $^{\circ}\mathrm{C}^{-1}$. The extrapolated resistivity at the melting point (156 °C) is 32.30 $\mu\Omega$ cm which compares favourably with most of the published values of 32.7,[3] 31.4,[4] 33.1,[8] 32.5[9] $\mu\Omega$ cm. The value of 29.1 $\mu\Omega$ cm quoted in the *Liquid Metals Handbook*[10] would seem to be too low. The temperature dependence $d\rho/dT$, given above as the constant B, is also in satisfactory agreement with published values of 2.45,[3] 2.53[8] and 2.85[9] $\times 10^{-8}$ Ω cm $^{\circ}\mathrm{C}^{-1}$ but the

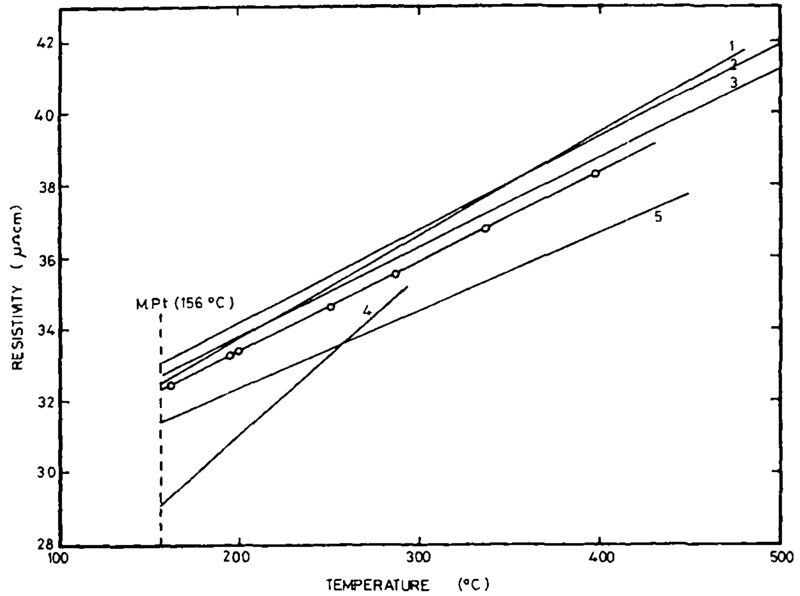

Fig. 1. Resistivity of liquid indium as a function of temperature.
○ Present work; 1. Takeuchi and Endo (Ref. 9); 2. Roll and Motz (Ref. 8); 3. Scala and Robertson (Ref. 3); 4. Ref. 10; 5. Goryaga and Belozerova (Ref. 4).

value of 4.45×10^{-8} Ω cm °C^{-1} given in Ref. 10 is again in disagreement with the other data.

Tin. Two purities of tin were investigated, Analar grade 99.9% pure, supplied by Hopkins and Williams, and S grade 99.999% pure, supplied by Capper Pass and Sons. The principal impurities present in these samples are listed in Table 1. The resistivity of the 99.9% pure sample increased linearly with temperatures between 258 °C and approximately 335 °C, least squares analysis giving the relation as:

$$\rho = 41.09\,(5) + 0.0276\,(4)T\ \mu\Omega\ \text{cm}.$$

At 335 ± 5° C the slope decreased abruptly by about 4% without a change occurring in the actual resistivity and, thereafter, the resistivity was given by the relation:

$$\rho = 41.56 + 0.0265\,(3)T\ \Omega\ \text{cm}.$$

The data are shown in Fig. 2 together with published data. The resistivity at the melting point (232 °C) determined by extrapolation of the linear portion of the curve below 335 °C was 47.50 $\mu\Omega$ cm. The resistivity of

TABLE 1 Sources and purities of the tin and lead used in the present work

Material	Source	Purity %	Principal Impurities
Tin	Capper Pass & Sons	99.999 Pass S	Sb, Pb, Cu, Fe, Bi, As, Ag
Tin	Hopkin & Williams Ltd.	Analar 99.9	Fe, Pb, Cu, Bi, Sb
Lead	Hopkin & Williams Ltd.	Analar 99.98	Ag, Cu, Fe, As
Lead	British Non-Ferrous Metals Research Association	99.999	Sn, Bi, Sb, As

Analar grade liquid tin has also been investigated by Adams[11] but, whilst the agreement with the present work is excellent at lower temperatures, no change of $d\rho/dT$ was reported and, consequently, above 335°C the resistivity deviates increasingly from the present values. The measurement of Goryaga[3] on liquid tin of unspecified purity are also in agreement with the present data below 335 °C but a very large decrease in $d\rho/dT$ of the order of 30% was reported at 520 °C; this was not confirmed in the present work during a preliminary run at temperatures up to 700°C and has not been reported in the other published measurements.[3,8,9,12]

The resistivity of the 99.999% tin also underwent a discontinuous decrease in its temperature dependence, as can be seen in Fig. 2, but at a lower temperature of 315 ± 5°C and the decrease (3.2%) was slightly smaller than that for the less pure sample. Below 315 °C, the resistivity is given by:

$$\rho = 40.88 + 0.0272\,(5)T \ \mu\Omega \text{ cm}$$

and above by

$$\rho = 41.16 + 0.0263\,(8)T \ \mu\Omega \text{ cm}.$$

The temperature at which the temperature coefficient changed was a constant regardless of whether the measurements were made when the temperature was being increased or decreased. The resistivity was consistently lower than that of the less pure sample by about 0.4 $\mu\Omega$ cm; this is somewhat greater than the increment of resistivity that would be expected for a 0.1% concentration of impurity. Scala and Robertson[3] also reported a

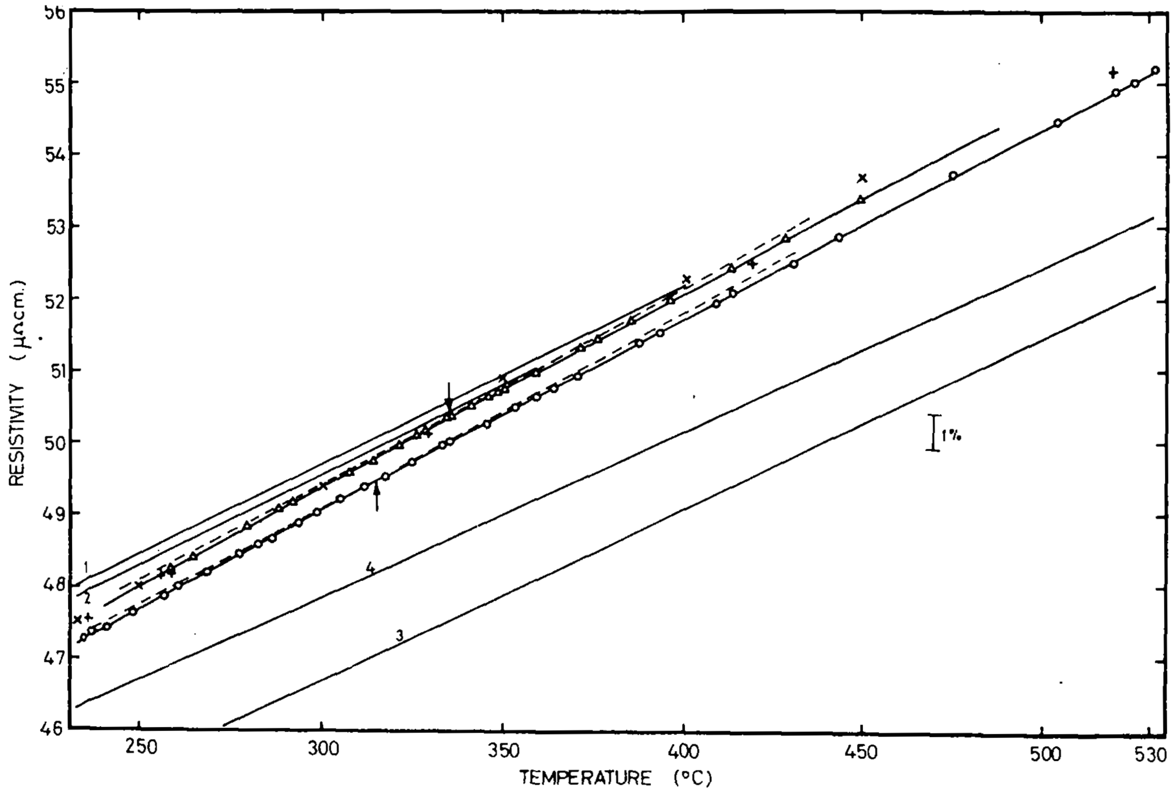

Fig. 2. Resistivity of liquid tin as a function of temperature. ○ Present work, 99.999% purity; △ Present work, Analar grade 99.9% purity; 0.5 mm. bore borosilicate capillary; + Present work, Analar grade: 1.0 mm. bore quartz capillary; × Adams, Analar grade (Ref. 11); 1. Roll and Motz (Ref. 8); 2. Scala and Robertson, 99.96% purity (Ref. 3); 3. Scala and Robertson, 99.996% purity (Ref. 3); 4. Takeuchi and Endo (Ref. 9).

dependence of resistance on the degree of purity for liquid tin but in their case the effect was considerably more pronounced, the resistivity of 99.996% pure material being roughly 5% lower than that of 99.96% purity. The resistivity extrapolated to the melting point is 47.20 $\mu\Omega$ cm; this, and the value for the less pure sample, fall within the spread of the published data—47.50,^{12} 48.0,^{8} 46.3,^{9} 47.85 and 45.1^{3} $\mu\Omega$ cm.

Lead. Two purities of lead were also investigated, namely 99.98% pure "Analar" grade, supplied by Hopkin and Williams Ltd., and 99.999% pure supplied by British Non-Ferrous Metals Research Association; the principal impurities in these samples are given in Table 1. The results of two runs on the high purity specimen and one run on the lower purity sample were in agreement to better than 0.05%; resistance/temperature plots are shown in Fig. 3 together with published data. Although this may indicate that the resistivity of lead is less dependent on the presence of small amounts of impurity than that of tin, the difference between the purities of the two samples of lead is a factor of 5 smaller than the difference between the impurity concentration in the tin samples studied. As

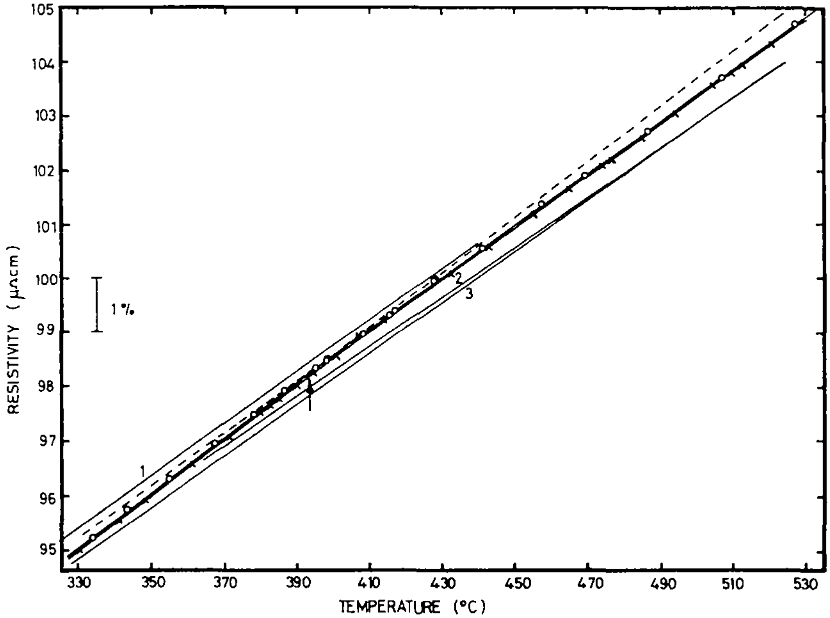

Fig. 3. Resistivity of liquid lead as a function of temperature.
○ Present work, 99.999% purity; × Present work, 99.98% purity; 1. Adams (Ref. 11); 2. Roll and Motz (Ref. 8); 3. Northrup and Suydam (Ref. 12).

for tin, a discontinuous decrease in the temperature dependence was observed, at a temperature of 393 ± 3 °C for all three runs. The resistivity of the 99.98% lead is given as follows:

Below 393 °C, $\rho = 78.21 + 0.0508\,(2)T$ $\mu\Omega$ cm
Above 393 °C, $\rho = 79.31 + 0.0480\,(4)T$ $\mu\Omega$ cm

The resistivity of the 99.999% pure sample is given as follows:

Run 1 below 393 °C, $\rho = 78.45 + 0.0501\,(1)T$ $\mu\Omega$ cm
above 393 °C, $\rho = 79.13 + 0.0484\,(1)T$ $\mu\Omega$ cm
Run 2 below 393 °C, $\rho = 78.27 + 0.0507\,(6)T$ $\mu\Omega$ cm
above 393 °C, $\rho = 79.36 + 0.0480\,(3)T$ $\mu\Omega$ cm.

The average decrease in the temperature dependence was about 4.9% which is greater than the change observed in tin. The resistivity at the melting point (327 °C) determined by linear extrapolation of the data below 390 °C is 94.85 $\mu\Omega$ cm which compares favourably with published values of 94.73,[12] 95.0[8] and 95.27[11] $\mu\Omega$ cm. The temperature dependence is very similar to the values observed in previous work which might indicate that the differences in absolute resistivities were due to small calibration errors. No change in temperature dependence has been reported by any of the previous workers.

Discussion

It is considered that the changes in $d\rho/dT$ observed in the present work are real and not due to errors in the measuring system for the following reasons:

1. A change of $d\rho/dT$ was not detected in pure indium, for which the cell and capillary used were the same as those for the runs on the tin and lead.
2. Different values of the transition temperatures were observed for liquid tin and lead using the same borosilicate cell. The transition temperature (335 °C) observed during a preliminary experiment in a fused quartz cell having molybdenum current electrodes and potential probes was similar to that observed with the borosilicate cell and tungsten electrodes reported here. It is therefore considered unlikely that the changes in $d\rho/dT$ are due to significant changes in the cell constants with increasing temperature.
3. The temperature measuring thermocouple was calibrated at the freezing points of pure tin, lead and zinc on completion of the

resistivity measurements and found to give agreement to within ± 0.5 °C with the established freezing points of the respective metals. These freezing temperatures cover the temperature range within which the irregularities occur and preclude the effects being due to a peculiarity of the thermocouple.

It is not easy to rationalise the observed changes of $d\rho/dT$ in lead and tin in terms of a common factor. In the case of tin, Hall coefficient measurements indicate, within the experimental scatter, a valence number of free electrons up to 420 °C.[13,14] However, there is a considerable body of experimental evidence to suggest that the liquid structure is abnormal and that structural changes take place within the range 80–200°C above the melting point. A subsidiary hump appears on the high-angle side of the main diffraction peak[15,16,17] which decreases in intensity and becomes more diffuse as the temperature rises. Although some controversy exists regarding the meaning of this, it has been interpreted by one group of workers[15] as indicating the existence of a short distance of interatomic approach corresponding to that in grey tin and that the liquid can be pictured as consisting of about 10% of clusters of tetrahedral grey tin-type bonds in dynamic equilibrium with liquid metallic tin. If this is a correct interpretation then the liquid might be expected to have a higher compressibility when the probability of the existence of such bonds is higher. On the theory of Takeuchi and Endo,[9] an increased compressibility would be accompanied by an increase in the temperature coefficient of resistivity which is what is observed in the present work, below the transition temperature. Velocity of sound measurements in liquid tin[22] do not, however, lend support to the posssibility of unusual compressibility changes above the melting point.

The theory of Ziman[19] gives the resistivity of a liquid metal as:

$$\rho = cf(V) \int_0^{2k_F} 4a(K) \mid U(K) \mid^2 K^3 \, dK$$

where c is a constant, $f(V)$ is a function of the atomic volume, $a(K)$ is the structure factor, $U(K)$ is the ionic pseudopotential, K is the scattering wave vector and k_F is the Fermi wave number. Since the integration limit $2k_F$ lies close to the subsidiary hump in $a(K)$, an additional contribution to the temperature dependence of resistivity might be expected as this hump becomes more diffuse with increasing temperature. A quantitative analysis to determine the magnitude of the contribution from this effect would require very precise diffraction data but published data are not sufficiently detailed for this purpose. Moreover, the diffraction data indicate that the subsidiary peak diminishes only gradually with increasing temperature and persists to high temperatures[15,20] whereas the slope changes observed in the present work appear to be abrupt, at specific temperatures. The present data do reveal a very slight tendency for curvature, convex toward the resistivity axis, but, if significant, it is not sufficient to account for the 3% or so difference between the temperature coefficient near the melting point and that at temperatures above 350 °C. If the effect was associated with changes in the energies of the core electrons then it would also be expected to influence the resistivity through a change in the ionic pseudopotential.

The thermoelectric power of a metal is intimately related to the electrical resistivity. Therefore, associated with any change in resistivity we would probably also expect unusual behaviour of the thermoelectric power and, indeed, this has been reported by Ubbelohde[21] over a temperature range of about 80 °C above the melting point, consistent with the present data.

Other properties which are particularly structure-sensitive show irregularities. One viscosity determination[22] on liquid tin indicated abnormally high values between the melting point and about 300° C; it was concluded from a thermodynamic analysis of these data[23] that clusters of about twenty atoms exist in the liquid in dynamic equilibrium with monomeric atoms. The observed non-linear temperature-dependence of the coefficient of self-diffusion[24] can also be attributed to groupings. The specific heat of liquid tin[25] initially decreases up to between 350 and 450 °C but thereafter rapidly increases, implying an unusual change in the vibrational energy distribution, and hence in the interatomic forces. A similar picture emerges from thermal conductivity measurements[26] which indicate decreasing conductivity between the melting point and about 300 °C. The higher value for the transition temperature for the less pure tin in the present work could, on the basis of the foregoing arguments in terms of atomic groupings or clusters, be due to the higher impurity concentration nucleating clusters at a higher temperature (as the temperature falls).

The change of $d\rho/dT$ which was observed in liquid lead cannot be so readily correlated with other phenomena. With one exception,[27] where a small subsidiary peak was observed on the high angle side of the first main peak in the range of 20 °C above the melting point, X-ray and neutron diffraction experiments indicate a simple monatomic structure.[28,29,30] The specific heat decreases linearly from the melting point to about 1000°C[25] and no abnormal viscosity behaviour has been reported. The evidence for a structural irregularity in this liquid is, therefore, slender and rests on the results of one diffraction experiment on a sample of unspecified purity.

A number of measurements of the Hall coefficient of liquid lead[13,31,32] indicate large but inconsistent deviations from the value that would be predicted from the valence of the metal, in contrast with the behaviour of most other liquid metals. Although the Hall effect in liquids is not yet fully understood, this deviation could be an indication that liquid lead has an abnormal electronic structure. On the other hand, optical measurements[33] indicate a number of free electrons only slightly greater than the valence. The inconsistency of the Hall coefficient data suggests that an experimental factor such as insufficient control over non-metallic, and especially oxygen, content of the liquid may be contributing to the large deviations from theoretical values. In the present work, great care was taken to remove surface oxide and to reduce the oxygen content of the argon atmosphere, before melting. The temperature at which the change in temperature coefficient occurred and the absolute resistivity were consistent for the three runs, although the magnitude of the slope change did vary slightly between runs.

Conclusions

The observed changes in the temperature-dependence of electrical resistivity in liquid tin are consistent with changes reported in many other physical properties of this metal. The observations seem to point to a structural irregularity in the liquid and the resistivity data suggest that this undergoes an abrupt change at about 100° C above the melting point. Although a structural anomaly is also indicated by diffraction experiments, the change with temperature appears to be gradual and the evidence suggests that the anomaly exists to several degrees above the melting point. It is not possible at present to draw firm conclusions about the nature of the anomaly on the atomic scale.

The resistivity change observed in liquid lead is also small and abrupt but apparently is not accompanied by changes in other bulk physical properties or in the structure.

The resistivity of liquid indium behaves normally, the resistivity being a linear function of temperature and the temperature coefficient a constant over the temperature range of the measurements.

A further study of the resistivities of liquid tin and lead in which the nature and concentration of impurities were carefully controlled might assist in clearing some of the points raised by the present work.

Acknowledgement

The authors wish to thank U.K.A.E.A. (Harwell) for financial support of this work and Professor J. G. Ball for providing laboratory facilities. One of us (H.A.D.) is also grateful to the U.K.A.E.A. for the award of a research stipend.

REFERENCES

1. Davies, H. A., and Leach, J. S. Ll., to be published.
2. Davies, H. A., and Leach, J. S. Ll., *Phil. Mag.* **19,** 1271 (1969).
3. Scala, E., and Robertson, W. D., *J. Metals* **5,** 1141 (1953).
4. Goryaga, G. I., and Belozerova, E. P., *Vest. Mosk. Univ.*, ser. Mat. Mekh. Astr. Fix. Khim. **13,** 133 (1958).
5. Goryaga, G. I., ibid. **11,** 79 (1956).
6. Ascarelli, P., *Phys. Rev.* **143,** 36 (1966).
7. Davies, H. A., Ph.D. Thesis, University of London (1966).
8. Roll, A., and Motz, H., *Z. Metallk.* **48,** 272 (1957).
9. Takeuchi, S., and Endo, H., *Trans. Jap. Inst. Metals* **3,** 30 (1962).
10. *Liquid Metals Handbook*, U.S. Office of Naval Research, Washington, D.C. (1952).
11. Adams, P. D., Ph.D. Thesis, University of London (1964).
12. Northrup, E. F., and Suydam, V. A., *J. Franklin Inst.* **175,** 153 (1913).
13. Greenfield, A. J., *Phys. Rev.* **135A,** 1589 (1964).
14. Takeuchi, S., and Endo, H., *Trans. Jap. Inst. Metals* **2,** 243 (1961).
15. Furukawa, K., Orton, B. R., Hamor, J., and Williams, G. I., *Phil. Mag.* **8,** 141 (1963).
16. Kaplow, R., Strong, S. L., and Averbach, B. L., *Local Atomic Arrangement Studied by X-Ray Diffraction*, ed. J. B. Cohen and J. E. Hilliard (Gordon and Breach, 1966).
17. Wagner, C. N. J., and Halder, N. C., *Adv. Phys.* **16,** 241 (1967).
18. Gordon, R. B., *Acta Met.* **7,** 1 (1959).
19. Bradley, C. C., Faber, T. E., Wilson, E. G. and Ziman, J. N., *Phil. Mag.* **7,** 865 (1962).
20. Wagner, C. N. J., and North, D. M., to be published.
21. Ubbelohde, A. R., *Proc. Roy. Soc.* **293A,** 291 (1966).
22. Yao, T. P., and Kondic, V., *J. Inst. Metals* **81,** 17 (1952–3).
23. McLaughlin, E., and Ubbelohde, A. R., *Trans. Faraday Soc.* **56,** 988 (1960).
24. Careri, J., *Nuovo Cim.* **1,** 517 (1965).

25. Misra, G., and Kumar, R., *Trans Indian Inst. Metals* **20**, 26 (1967).
26. Pashaev, B. P., *Soviet Physics, Solid State* **3**, 306 (1961).
27. Kruschev, B. I., Bogomolov, A. M., and Sharipova, L. S., *Fis. Metal Metalloved* **22**, 279 (1966).
28. Sharrah, P. C., and Smith, G. P., *J. Chem. Phys.* **21**, 228 (1953).
29. Sharrah, P. C., Petz, J. I., and Kruh, R. F., *J. Chem. Phys.* **32**, 241 (1960).
30. Kaplow, R., Strong, S. L., and Averbach, B. L., *Phys. Rev.* **138A**, 1336 (1965).
31. Busch, G., and Tièche, Y., *Phys. Kondens. Materie* **1**, 78 (1963).
32. Draper, P. H., Unpublished results, Imperial College (1969).
33. Hodgson, J. N., *Phil. Mag.* **7**, 229 (1962).