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Contents:

	<u>Page</u>
<u>PHYSICS</u>	
Thermal and Magnetic Properties of Alloys at Low Temperatures	14
Electronic Band Structure in HCP Metals	15
<u>CHEMISTRY</u>	
Properties of Clathrates	17
Iron Complexes	17
Thermodynamics of Clathrates	18
<u>METALLURGY</u>	
Plastic Properties of Polycrystalline Hexagonal Metals	19
Method for Determining Austenitic Grain Size	21
<u>BIOSCIENCES</u>	
Megaloblastic Anemia in Africans	22
The Electrical Properties of Denervated Skeletal Muscle	22
Minute to Minute Changes in Cardiac Output by the Direct Fick Method in Normal Subjects During Exercise and Recovery	23
<u>MISCELLANEOUS</u>	
Personal News Items	24
International Photobiological Congress	24
Forthcoming Meetings in Europe	25
Personnel of the Office of Naval Research, Branch Office, London	26

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THERMAL AND MAGNETIC PROPERTIES OF ALLOYS AT LOW
TEMPERATURES

Drs. F. E. Hoare and J. C. Matthews (University of Leeds) have now completed their measurements of specific heats and magnetic susceptibilities in Pd-Ag and Pd-Rh alloys down to liquid hydrogen temperature (cf. ESN 7, 115 (1953), and Proc. Roy. Soc. A216, 502 (1953)), and are extending the measurements to liquid helium temperature as well as to other alloy systems. The thermal and magnetic properties of the palladium alloys have been determined as a function of temperature up to 300°K and as a function of concentration of the alloying element (Ag or Rh). The results of the study show that χ_0 (the value of the susceptibility at 0°K as extrapolated from the curves) for the Pd-Ag alloy decreases with increasing Ag concentration, but increases for Pd-Rh with increasing Rh concentration. Since pure Rh has a smaller magnetic susceptibility than Pd, the above result substantiates the assumption of a common d-band for these alloys.

Pure palladium and alloys with up to 3 per cent of either Ag or Rh show a maximum in χ/χ_0 at about 90°K, the most pronounced maximum occurring for almost pure Pd. The maximum in the χ/χ_0 versus temperature curve for these alloys sheds considerable light on the shape of the d-band, indicating a density of states versus energy curve which is concave upward.

Drs. P. Rhodes and E. W. Eiccock (University of Leeds) have derived theoretical expressions for the magnetic and thermal properties of partially filled bands

according to the collective electron model. Assuming a density of holes of the form $N(\epsilon) = \alpha_0(1 + \alpha\epsilon^n)$ where ϵ is measured from the top of the band, they found the best fit with Hoare and Matthew's data for $n = 3$. In order to observe a maximum in the χ/χ_0 vs temperature curve, n must be greater than one, and α must be appreciably greater than zero but less than $(n - 1)$. A paper by Elcock, Rhodes, and Teviotdale on this subject will appear shortly in the Proceedings of the Royal Society.

The measurements of magnetic susceptibility were made with a Sucksmith ring balance and were performed by using a temperature-drift method, i.e. the susceptibility was measured at preassigned temperatures while the specimen was warming up. The specimen was situated in a small glass container, which after evacuation was filled with 5 cm He gas as a heat-transfer agent, the temperature being measured by a thermocouple in direct contact with the specimen. The photographic method for recording readings of the Sucksmith balance, as previously described (Hoare and Matthews, Proc. Roy. Soc. A212, 137 (1952)), has been discarded in favor of a rapid direct-reading one, in order to eliminate the time-consuming job of reading the photographic film. The new method employs a split photocell which, by means of servomotors, follows the light beam from the Sucksmith balance. The photocell is moved up and down by means of a worm gear, the revolutions of which are counted with a mechanical counter, and give an accurate measure of the displacement of the specimen in the magnetic field.

Thermal and magnetic measurements are now being made on Pt-Ir and Mn-Cu alloys.

ELECTRONIC BAND STRUCTURE IN HCP METALS

Dr. P. Rhodes (University of Leeds) has made several approximate calculations of the band structure of hexagonal-close-packed metals with particular application to titanium. This work was done preliminary to a study of Ti by the cellular method, which is being carried out by Mr. Shiff (Imperial College, London). One of the calculations performed by Rhodes is the

tight-binding approximation in which the one-electron wave functions are expressed as

$$\psi = \sum_n e^{i\mathbf{k}\cdot\mathbf{r}} a(\mathbf{r}-\mathbf{r}_n),$$

where the a 's are atomic functions; only nearest neighbor interactions were considered. This approximation has yielded a density of states curve as shown in Fig. 1(a). The first discontinuity in the slope of the $N(E)$ versus E curve is caused by the energy surface touching the prism face of the Brillouin zone; the fact that $N(E)$ becomes infinite at the top of the band is due to a defect in the model, probably arising because only nearest neighbor interactions are considered.

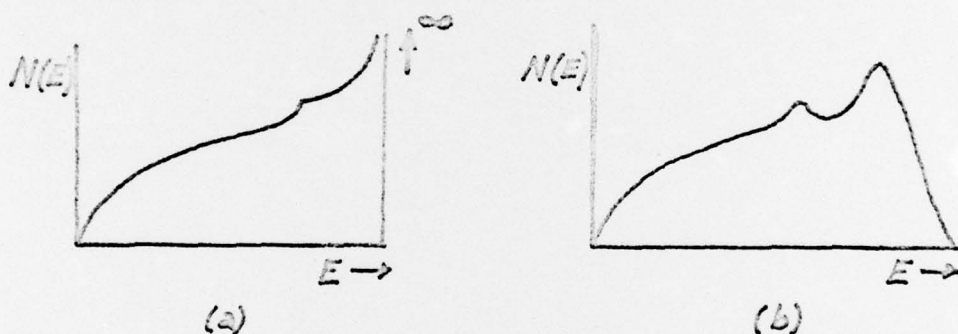


Fig. 1. Density of states, $N(E)$, versus energy, E .
 (a) Tight binding approximation,
 (b) Nearly free electrons.

A further calculation using the nearly free electron approximation yielded a density of states curve shown in Fig. 1(b); in order to get the detailed shape of the $N(E)$ curve, a few assumptions had to be made such as an approximate width for the forbidden zone of 2-5 ev.

The cellular calculation being performed by Shiff uses the method of von der Lage and Bethe as improved by Howarth and Jones (Proc. Phys. Soc. A65, 355 (1952)). Since this method gives information only

for a few electrons with specified wave vectors, Rhodes suggests that approximate calculations, such as those described above but carried out in terms of arbitrary parameters, can be used in conjunction with the cellular method to get more information about the band structure of multivalent metals.

PROPERTIES OF CLATHRATES

Several laboratories in Oxford are investigating the occlusion compounds formed by quinol, and by other substances, with various gases. Mr. H. M. Powell and his collaborators of the Chemical Crystallography Department are studying the crystal structure and stereochemistry of several types of such occlusion compounds, while thermochemical measurements are being made by Dr. R. E. Richards (Physical Chemistry Laboratory), and low temperature studies are in progress in the Clarendon Laboratory.

Powell has found that the available spaces in tri-*o*-thymotide crystals consist of channels which are capable of accommodating carbon chains up to about five or six carbon atoms (cf. J. Chem. Soc. 3747 (1952)). Occlusion compounds of tri-*o*-thymotide with longer carbon chains have recently been prepared; these, however, are hexagonal rather than trigonal as before. Paraffin chains containing 17 carbon atoms have been occluded.

Iron Complexes

Hexamethylcarbylamine ferrous chloride, $[\text{Fe}(\text{CNCH}_3)_6]\text{Cl}_2$, possesses a structure which is capable of accommodating four water molecules for each parent molecule. X-ray analysis indicates that these are randomly distributed, probably because of the strong electrostatic attraction between the iron and the chloride ions.

Messrs. E. Wait and H. M. Powell have observed an interesting structure for the occlusion compound of the fully covalent dicyano-tetra-methylisonitrile iron, $[(\text{CH}_3\text{NC})_4\text{Fe}(\text{CN})_2]$, with six molecules of water. The substance can exist in cis and trans forms depending on

the relative orientation of the two CN groups which are not coordinated with methyl groups. The cis form of this substance is easy to obtain and forms a hexahydrate occlusion compound which loses water extremely readily. X-ray analysis indicates that the water molecules in this occlusion compound are present in chains of six molecules connected by very long hydrogen bonds, about 3 - 3.1 Å, suggesting that the water is in a "quasi vapor" condition.

Thermodynamics of Clathrates

The thermodynamics of the clathrates presents some subtle problems. Recent experiments by Richards confirm and generalize the observations of W.F.K. Wynne-Jones (cf. *Changement de Phases*, Ed. Soc. Chim. Phys., Paris (1953)) that these substances have equilibrium vapor pressures which are generally approached extremely slowly. It was found that the NO clathrate of quinol builds up an equilibrium pressure of over an atmosphere in a sealed tube. The argon clathrate loses weight with time and this loss is apparently proportional to the surface exposed. Thus the large crystals generally used in X-ray studies show this loss only to a very slight extent. It is planned to investigate the equilibrium vapor pressure of various clathrates and thus get the free energies of formation of these compounds. This, with the measured heats of formation, will yield entropies of formation, and these should throw additional light on their structures.

The calorimetric heats of formation are directly proportional to the amount occluded, indicating that there is no significant interaction between the individually occluded molecules (cf. ESN 6, 206 (1952)). This makes them useful model substances for physical studies. The magnetic susceptibilities of the oxygen and NO clathrates were determined at room temperatures by Richards (cf. *J. Chem. Soc.*, 3295 (1952)) and at very low temperatures by Dr. R. H. Cooke et al in the Clarendon Laboratory. The measurements were in good qualitative agreement with theoretical predictions but the quantitative agreement in the helium range is not yet entirely satisfactory. It is possible that the electrostatic field of the lattice has an effect which will have to be accounted for.

The importance of the surface in occlusion compounds is also indicated by some recent experiments of Prof. M. v. Stackelberg (Bonn). He finds that in the hydrates of various organic chloro compounds, e.g. CHCl_3 , $\text{C}_2\text{H}_5\text{Cl}$, etc., the lattice of H_2O molecules contains two types of holes. The organic molecules fit into the large holes, while the small holes are empty. Preparing these solid hydrates under inert gas pressure (CO_2 , N_2 , etc.) a more stable solid with a higher decomposition temperature is obtained. The inert gas molecules fill the holes in the surface layer(s) and this apparently increases the stability.

PLASTIC PROPERTIES OF POLYCRYSTALLINE HEXAGONAL METALS

Dr. S. F. Pugh (A.E.R.E., Harwell) has considered theoretically the plastic properties of polycrystalline hexagonal metals, particularly in relation to the elastic moduli. The plastic deformation of metals at temperatures which are low relative to the melting point is believed to occur entirely by the dislocation mechanism, and therefore the calculations of dislocation theory are applicable. By this approach the following relationship was derived:

$$\frac{1}{H} = \frac{c}{G b}$$

where H is the Brinell hardness (a measure of the resistance to plastic deformation), G is the elastic shear modulus for the material, b is the Burgers vector of the dislocation, and c is a constant for all metals of the same crystal structure. This relationship indicates that the quantity

$$\frac{G b}{H}$$

should be a constant for all hexagonal metals.

The plasticity of metals can be considered in terms of two components. The first of these, discussed above, is due to movement of dislocations and is a function only of elastic moduli and lattice dimensions. The second component is due to thermally activated

processes and is a function of temperature and strain rate. Rigorously, therefore, the above equation should include another term to take into account the fact that for a fixed temperature of measurement, some metals are much closer to their melting points than others. This additional term, which would be very important for low melting point metals, is extremely complex because it deals with, among other factors, the interaction of vacancy diffusion and dislocations.

Utilizing data from the literature as well as results from his own laboratory, Pugh has calculated the quantity

$$\frac{G b}{H}$$

for the hexagonal metals and compared the values for constancy. These results are summarized in the following figure.

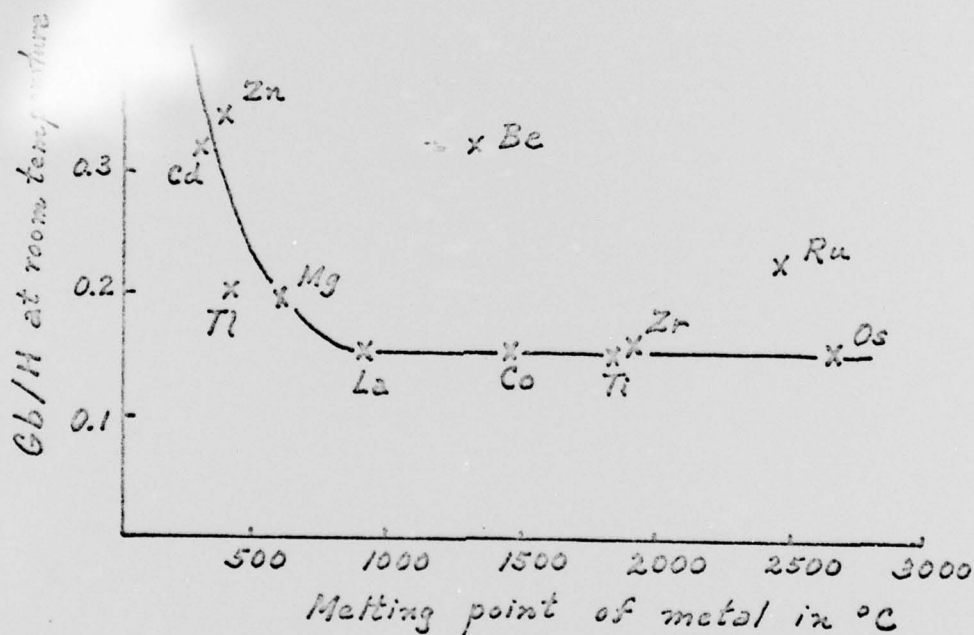


Fig. 1. Plot of Gb/H for the hexagonal metals.

which shows that

$$\frac{G b}{H}$$

is constant for hexagonal metals which melt above 1000°C. In metals which melt below this temperature the thermally activated processes play an increasing role in the room temperature plastic behavior.

The case of beryllium is an interesting discrepancy in the above plot. The entire theoretical treatment was based on the assumption that the principal mode of plastic deformation is slip, whereas it is known that beryllium deforms mainly by twinning.

Pugh has also considered the malleability of the hexagonal metals and the relation of this property with the elastic moduli. A high value of K, the bulk modulus, corresponds to a high resistance to fracture, and a low value of G, the shear modulus, represents a low resistance to flow. Thus the ratio K/G is indicative of the malleability. For example, the metals Hf, Zn and Ti have high K/G ratios and are malleable, whereas Be and Os have low ratios and are brittle.

METHOD FOR DETERMINING AUSTENITIC GRAIN SIZE

Mr. A. Kohn (I.R.S.I.D., St. Germain-en-Laye) has developed a new metallographic technique for the determination of austenitic grain size in steels. This method, unlike the standard one, has the advantage that it does not introduce foreign elements into the steel during the course of austenitizing which can affect the kinetics of austenitic grain growth.

A previously polished specimen is austenitized in an argon atmosphere, and at the end of this treatment its surface is very lightly oxidized by an air jet. The specimen is then quenched, repolished very lightly, and etched with one of the usual reagents (Nital, Villela's, etc.) to reveal the boundaries of the prior austenite grains which had been very slightly enriched in oxygen.

Kohn has successfully applied this technique to a wide variety of steels with different compositions.

The method and apparatus, which are very simple, should be quite useful in the metallography of steels.

MEGALOBlastic ANEMIA IN AFRICANS

Drs. Henry Foy and Athena Kondi of the Wellcome Trust Laboratories, Nairobi, Kenya, in a paper presented at a meeting of the Royal Society of Tropical Medicine and Hygiene, London, described 25 cases of non-pernicious megaloblastic anemia in Africans which were cured when the patients were treated either orally or by intramuscular injections of penicillin. They pointed out that this is but another instance of the interrelationship between the intestinal flora and fauna of the gut and anemia. For instance, the anemia associated with Diphyllobothrium latum can usually be cured by the removal of the worm, and sometimes by administering Vitamin B 12. The dry worm contains large amounts of this vitamin which must have been obtained by depriving the host of this substance. In addition, antibiotic supplements when added to the diets of animals usually produce growth acceleration but if continued for long periods of time may cause vitamin deficiencies and subsequent megaloblastic anemia. Foy and Kondi believe that the biosynthesis of the flora of the gut is very important and that probably the mode of action of the penicillin is to cause lysis of the bacteria with release of the elements which are needed to cure the anemia.

THE ELECTRICAL PROPERTIES OF DENERVATED SKELETAL MUSCLE

Mr. J. G. Nicholls of the Biophysics Department at University College, London, has been investigating the changes in the passive electrical properties of skeletal muscle following denervation. The changes in the muscle constants are listed in Table 1. These results are the average of thirteen experiments.

It was found that the resting and action potentials measured by intracellular electrodes were unchanged by denervation. However, the minimum current required to stimulate was reduced to 1/3 after denervation and there was a reduction in the critical depolarization

at which impulses are initiated. The threshold dose of acetylcholine to produce action potentials is reduced by a factor of one hundred. The depolarization with threshold doses of ACH is limited to a region corresponding to the end-plate in the normal muscle. At other regions of the muscle the acetylcholine requirement for depolarization is 10^4 times as great as normal.

TABLE 1

Muscle	λ Length Constant mm	T Time Constant msec	R_i Internal Re- istance Ω -cm	R_m Membrane Re- istance Ω -cm ²	C_m Membrane Capacity $\mu F/cm^2$	Acetyl- choline Threshold μg
De- nervated	1.46	29.3	350	10300	3.1	8×10^{-9}
Normal	1.00	17.2	328	4970	4.1	8×10^{-7}

MINUTE TO MINUTE CHANGES IN CARDIAC OUTPUT BY THE DIRECT FICK METHOD IN NORMAL SUBJECTS DURING EXERCISE AND RECOVERY

Drs. J. M. Bishop, K. W. Donald and G. L. Wade of the Department of Medicine at the Queen Elizabeth Hospital in Birmingham have used the direct Fick method of determining cardiac output in the determination of how soon a steady state is reached during heavy exercise. Subjects were exercised in a horizontal position on a bicycle ergometer which permitted a constant level of working. Expired air was collected in a Tissot spirometer and was automatically sampled from the collecting tube at a constant rate. Arterial blood was sampled at one minute intervals and the mixed venous samples from the pulmonary artery were taken four times a minute during the five minutes of exercise and five minutes of recovery. Four levels of working were studied. These correspond to oxygen consumption values of 295, 398, 561 and 1046 milli-

liters per minute per square meter of body surface. Sixteen subjects, aged 20 to 52 years, were studied, three males and one female at each level of working.

It was found that after approximately one minute of exercise the mixed venous blood oxygen saturation and the cardiac output had reached a steady state in all except one subject - a female doing the heaviest work. Cardiac output increased proportionately to the oxygen consumption and at a rate of approximately 0.51 liters of blood/min. m^2 per 100 cc of oxygen/min. m^2 . During recovery a steady state was reached within one minute after cessation of work except in the group doing the heaviest exercise. There was a rise in mean pulmonary artery pressure roughly proportional to the cardiac output. The highest value recorded was 52 mm Hg.

PERSONAL NEWS ITEMS

Professor Sir Lawrence Bragg has accepted the position of Director of the Davy-Faraday Research Laboratory at the Royal Institution, London. The appointment is effective as of 1 January.

Professor N. F. Mott will leave Bristol University on 1 August to become Cavendish Professor of Experimental Physics at Cambridge, the position vacated by Sir Lawrence Bragg.

Dr. D. D. Eley, Lecturer of Biophysical Chemistry at Bristol University, has accepted the position of Professor of Physical Chemistry, University of Nottingham, a newly created chair. His duties will begin on 1 August.

INTERNATIONAL PHOTOBIOLOGICAL CONGRESS

The International Photobiological Congress will be held in Amsterdam on August 23 - 28, just preceding the meeting of the International Society for Cell Biology in Leiden. Dr. Raymond Latarjet of the Institute of Radium, 26 rue d'Ulm, Paris, has been asked to arrange a

symposium for the Photobiology Congress on the subject of "The Effects of Non-Ionizing Radiations on Genetic Elements of Cells". Those interested in participating or receiving further information should communicate directly with Dr. Latarjet.

Two other symposia will be held at the Congress, (1) "Photoperiodism in Plants and Animals" with Dr. R. van der Veen (Eindhoven) as Chairman, and (2) "The Fundamental Effects of Light on the Skin" with Professor James Hardy (Philadelphia) as Chairman.

For general information enquiries should be addressed to: Secretariate Congres C.I.P., Radio-logisch Laboratorium, Wilhelminagasthuis, Amsterdam.

FORTHCOMING MEETINGS IN EUROPE

The following is a list of the more important forthcoming events in Europe for 1954, compiled according to information available as of 15 December 1953.

<u>Date</u>	<u>Meeting</u>	<u>Place</u>
24-26 March	Symposium on Chemistry and Physics of Synthetic Fibers	London
1 - 5 April	Annual Conference, British Psychological Association	Nottingham
5 -10 April	Annual Meeting, Ergonomics Research Society	The Hague
6 - 9 April	The Institute of Physics, Conference on the Physics of Particle Size Analysis	Nottingham
7 - 9 April	The Study of Fast Reactions, The Faraday Society	Birmingham
7 -10 April	Conference on Luminescence	Cambridge
23-25 April	Italian Society of Geophysics and Meteorology, 2nd General Assembly	Genoa

FORTHCOMING MEETINGS IN EUROPE, Cont.

<u>Date</u>	<u>Meeting</u>	<u>Place</u>
27 April- 6 May	Institute of Metals and French Metallurgical Society, Joint Meeting	London
21-22 May	Congress of International Society of Surgery	Paris
1 - 9 July	British Medical Association	Glasgow
6 -10 July	Joint Commission on Electron Micro- scopy of the International Council of Scientific Unions	London
6 -16 July	International Union of Biological Sciences 8th International Botani- cal Congress	Paris
6 -17 July	International Union of Pure and Applied Physics, 8th General Assembly	London
13-17 July	Symposium on Solid State (to follow I.U.P.A.P.)	Bristol
13-17 July	Symposium on Experimental Nuclear Physics (to follow I.U.P.A.P.)	Glasgow
12-22 July	International Gerontological Congress	London and Oxford
15-19 July	International Conference on Thrombosis and Embolism	Basle
19-24 July	Radioisotope Conference, arranged by A.E.R.E., Harwell	Oxford
21-24 July	International Congress for Psycho- therapy	Zurich
21-28 July	International Union of Crystal- lography	Paris

FORTHCOMING MEETINGS IN EUROPE, Cont.

<u>Date</u>	<u>Meeting</u>	<u>Place</u>
26-31 July	International Congress on Obstetrics and Gynecology	Geneva
28 July- 2 August	International Union of Theoretical and Applied Mechanics	Brussels
Summer	Commission of Macromolecular Chemistry of the International Union of Pure and Applied Chemistry	Milan
Summer	4th International Sedimentological Congress	Esbjerg, Denmark
14 August	5th International Congress of Mental Health	London
16-18 August	Joint Commission on Ionosphere of the International Council of Scientific Unions	Brussels
23-28 August	International Congress for the Philosophy of Science	Zurich
23-28 August	International Photobiological Congress	Amsterdam
23 August- 2 September	International Scientific Radio Union, 11th General Assembly	Amsterdam
30 August- 3 September	International Congress of Orthopedic Surgery and Traumatology	Berne
30 August- 6 September	5th International Spectroscopy Colloquium	Salzkammergut, Austria
30 August- 9 September	International Union of Mathematics	The Hague
2 - 9 Sept.	International Society for Cell Biology	Leiden