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# THE MAGNETIC PROPERTIES OF CHROMIUM

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ABSTRACT. Pure chromium has been prepared from chromium amalgam and its magnetic susceptibility has been studied over the temperature range 90 to 620° K. The mass susceptibility is practically constant over this range, the slight departures from constancy being partially explainable by the effects of thermal expansion on the experimental results. The mean susceptibility is  $3.08 \times 10^{-6}$  e.m.u. per gram at room temperature. The effects of impurities on the magnetic behaviour of chromium, which are very pronounced in the case of samples prepared at lower temperatures, are considered in detail, and the thermal and magnetic data for this element are discussed on the basis of modern theories of paramagnetism of metals.

#### § 1. INTRODUCTION

HROMIUM belongs to the first transition group of elements and its magnetic properties are, therefore, of considerable interest; yet a survey of the literature shows that they have been somewhat inadequately investigated. For example, the value of the susceptibility per gram given in the International Critical Tables is  $3.7 \times 10^{-6}$  c.c.s. units, derived from the work of Honda<sup>(1)</sup>. An examination of the curves of susceptibility plotted against H shows conclusively that the materials used were markedly ferromagnetic, and indeed the chemical analysis given in Honda's paper includes the statement that the chromium used by him contained 2 per cent of iron. This is extraordinarily large and is probably an overestimate in view of the properties we have found specimens of chromium to possess in the present investigations. Again, in Owen's work<sup>(2)</sup> the amount of iron stated to be contained in his specimen of chromium was 5.3 parts per 1000, and the value of  $\chi$  is given as  $3.175 \times 10^{-6}$  in a field of 26,000 oersteds, and  $2.87 \times 10^{-6}$  when extrapolated to the value in an infinitely large field. We must conclude, then, that pure chromium has so far not been investigated. This is a little surprising in view of the manner in which chromium is so readily produced in large-scale electrolytic processes for use in commerce, but it must be remembered that such preparations contain large amounts of occluded gases, notably oxygen and hydrogen, which are inseparable from the method of manufacture, and no particular care is exercised to avoid the presence of traces of iron.

In some recent work, Bates and Reddi Pantulu<sup>(3)</sup> examined the properties of amorphous manganese and showed that this element could be prepared in a nonferromagnetic state in spite of its well-known tendency to combine with other elements to form ferromagnetic compounds. It therefore seemed to us to be of interest

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to prepare specimens of pure chromium by the same method for a survey of its magnetic properties. It is generally assumed that the preparation of chromium amalgam is much easier than the preparation of manganese amalgam, but in our work we found that the former preparation was attended with considerable difficulties, although we eventually succeeded in preparing specimens of the material which we regarded as satisfactory for the purposes of our investigations.

## §2. PREPARATION OF MATERIAL

Concentrated solutions of chromic sulphate,  $Cr_2(SO_4)_3.7H_2O$ , were prepared from the salt obtained from Hopkins and Williams, or from green flakes of specially pure chromium sulphate obtained from Merck, or from the violet powder supplied by British Drug Houses Ltd.; the first product was found the best for our purposes. To each litre of solution 7 cm<sup>3</sup> of sulphuric acid was added. The solution was then electrolyzed, a platinum plate being used as anode and a pool of mercury as cathode. During the course of electrolysis the strength of the solution was maintained by the periodic addition of chromic sulphate crystals. Currents of approximately 14 A., corresponding to a current density of  $1 \cdot 1 A./cm^2$  at the cathode, were usually passed for some 100 minutes. These produced satisfactory amalgams, but it was found that higher current-densities produced a flaking of the amalgam surface or a partial breakdown of the amalgam, apparently with the deposition of crystalline chromium, in addition to excessive heating of the solution. The latter was contained in a thinwalled glass vessel placed in a container through which cold water circulated.



Figure 1. Apparatus for distillation of chromium amalgam.

The electrolysis was accompanied by the copious evolution of hydrogen, and slight stirring of the mercury surface was desirable. The amalgams were rather thin and quite unlike the pasty type obtained with manganese. They did, however, contain some lumps rich in chromium which were easily dispersed throughout the main body of the liquid. Now, one of the main difficulties which accompanied the handling of the amalgam lay in the fact that chromium amalgam is unstable in the presence of non-acidulated water; consequently it could not be washed in the usual manner, and it had to be washed several times with absolute alcohol for the best results, although preliminary washing with water and later washing with absolute alcohol was also tried in the case of a few preparations.

The amalgam was introduced into the bulb of the pyrex glass apparatus shown in figure 1, which is somewhat similar to that employed in the earlier work, but the present design was made for the more efficient handling of large volumes of amalgam and their subsequent treatment. The vessel was first evacuated through a short piece of new rubber pressure tubing which was then clipped, detached from the pump, and provided with a funnel whose exit tube was suitably narrowed. The funnel was lined with filter paper, and when the amalgam was placed in it, any residual alcohol

could condense, and drying tubes; liquid-air traps and a mercury-vapour pump

or slight impurity formed by washing came to the surface. The clip was opened and the amalgam stirred slowly as it trickled into the apparatus, impure portions being effectively shut out by closing the clip at the proper time. All these operations were carried out as quickly as possible, and, in our view, the success of the preparation depends upon the rapidity with which they are performed. The apparatus was then speedily connected to a Hyvac pump through a cooled vessel, in which mercury

were later brought into use. The mercury was at first boiled off fairly rapidly, for in this way any film of oxide on its surface was carried over into the condenser. In the early experiments the temperature was not raised above 400° C., and when the removal of mercury had been as far as possible completed the glass apparatus was sealed at the constriction c, figure 1. The bulb A now contained the several pyrex glass beads and a mass of chromium. This mass was exceedingly hard and its pulverization with the glass beads was practically impossible; the bulb A was therefore broken and the substance readily powdered with a glass rod and introduced into a new apparatus similar to that of figure 1. This was evacuated with a mercury-vapour pump and heated to about 400° C. for about three hours. The powder was then forced into the tube t through the constriction d which was afterwards sealed. This was the mode of preparation of specimens similar to no. I. It should be mentioned that when the bulb A was broken, some slight pyrophoric action between the air and the traces of powdered chromium inside occurred, but there was no trace of such action with the main mass of the specimen which we used in our measurements. Measurements made with specimens like no. I showed that the temperature 400° C. was not sufficiently high to remove all traces of mercury and hydrogen occluded during electrolysis. The effects of such occlusions will be described below. In later experiments we therefore raised the temperature of the bulb A and its contents to  $500^{\circ}$  C. and maintained it for four hours. It was also found that when the temperature was raised to 500° C. the chromium yield was easily powdered in situ without the necessity of breaking the bulb A. In this way specimens like no. IX were prepared, and we are therefore disposed to regard such specimens as the purest obtained. It was usually found convenient to seal the apparatus at the constriction e, and then to powder the chromium. The apparatus was next connected to the pumping system by slipping rubber pressure tubing over the seal at e, and, when the pumps were effectively running, connexion was made to the bulb A by breaking the glass at a file mark previously made near the seal e. The temperature of the powder was then raised, and it was found, in agreement with the work of Makariewa and Birükoff<sup>(4)</sup>, that hydrogen was copiously evolved in the region of 580° C. This was the treatment given to the specimen no. IX, which was maintained at the highest temperature permissible with pyrex glass under atmospheric pressure until no more evolution of gas could be detected by means of a vacuum tester. Specimen no. IX may be regarded as reasonably free of mercury, hydrogen and oxide, and we do not think it possible with present technique to obtain a much purer specimen with this temperature treatment.

### **§3. MAGNETIC MEASUREMENTS**

The sealed tube t containing the specimen was provided with hooks and suspended vertically from one arm of a sensitive chemical balance and measurements were made by the Gouy method. To the lower end of the tube t was attached an evacuated pyrex tube of the same dimensions, in the manner described in the previous paper by Bates and Reddi Pantulu<sup>(3)</sup>. The lower end of the specimen was thus placed in a uniform magnetic field H while its upper end was in a practically field-free space when the electromagnet was excited. The pull exerted on the specimen by the magnetic forces was then given by

## $mg = \frac{1}{2}k\alpha H^2$ ,

where  $\alpha$  is the area of cross-section of the tube *t*, and *m* the difference between the masses in the pan of the balance when the field was off and when it was on. Corrections for the magnetic effect of the air surrounding the suspended system and for the glass were avoided by the use of the lower evacuated tube.

The quantity k in the above expression represents the volume susceptibility of chromium as packed in the tube; hence, to find the mass susceptibility the packing density was found later. The absolute accuracy of the results depends on the uniformity of the cross-section  $\alpha$ ; the tubes were selected with care and measured prior to use, the value of  $\alpha$  being finally obtained by direct measurement after removal of the chromium. Determinations of k were made over the range of temperature -183 to  $350^{\circ}$  C. For the high-temperature measurements the furnace arrangement used by Bates and Reddi Pantulu was employed, but the work was greatly facilitated by the addition of a special water jacket placed between the pole pieces to maintain the latter at a uniform temperature and to stabilize the furnace temperatures. The construction of this water jacket is shown in figure 2. It was



Figure 2. Diagram of water jacket for furnace.

made of thin sheet brass soldered to a frame with solid ends, as shown in the left part of the figure. The water was forced to flow evenly through the side wings by a perforated baffle around the middle, indicated by the broken line, so that the whole jacket was maintained at a uniform temperature.

For the measurements at carbon-dioxide and liquid-oxygen temperatures the specimen was suspended inside a copper tube, with a piece of rubber tubing fitted to its upper end and mounted inside a Dewar flask containing carbon dioxide snow or liquid oxygen. In one or two cases the tube was replaced by a very thick copper block which was first cooled by liquid oxygen, after which its temperature rose

H

784

k

 $\alpha, m$ 

slowly, and at a convenient temperature recorded by a thermocouple a magnetic measurement was taken; this was not really satisfactory and the accuracy of such measurements was not high, but they provided very valuable checks upon the results obtained at other temperatures.

## §4. EXPERIMENTAL RESULTS FOR LOW-TEMPERATURE PREPARATIONS

In view of the foregoing remarks, the results obtained with specimen no. IX will be described first. In common with every specimen so far made, this specimen exhibited traces of ferromagnetism. Consequently in all our determinations we applied the Owen-Honda correction, using the equation



Figure 3. Specimen no. IX. Graphs showing  $mg/H^2$ , which is a measure of susceptibility, as a function of r/H.

where  $\sigma$  is the saturation specific magnetization of the impurity. A typical set of determinations is shown in figure 3, where the magnetic pull divided by  $H^2$  is plotted

\* This equation is generally written  $\chi_{\infty} = \chi_H - \sigma/H$ , but in this form it can only be used with measurements in which small spherical specimens are placed in a non-uniform field, where H.dH/dx is involved. The derivation of the correct formula for use with the Gouy method was first made by  $Vogt^{(5)}$ .

as a function of I/H for a series of different temperatures. The intercept at I/H=0 gave the true value of the susceptibility of the paramagnetic material. It was not found necessary to apply the more complicated form of correction suggested by  $Vogt^{(s)}$ . At the same time it should be pointed out that this assumes that the ferromagnetism is due to an impurity or rather to a compound of chromium and an impurity, and not due to pure chromium; this is a matter which will be discussed further. It is, of course, possible to obtain from the curves shown in figure 3, the magnitude of the ferromagnetic correction at each temperature.

The values of  $\chi$ , the susceptibility per gram of chromium for specimen no. IX, are shown in figure 4, together with the corresponding values of  $1/\chi$  and the ferromagnetic correction  $2\sigma$  obtained from the lines of figure 3. The value of the mass susceptibility at the room temperature is  $3.21 \times 10^{-6}$  at  $20^{\circ}$  C., which is some 10 per



Figure 4. Specimen no. IX. Maximum temperature during preparation,  $600^{\circ}$  C. Graphs of  $\chi$ ,  $1/\chi$  and  $2\sigma$  as functions of temperature.

cent lower than that given by Honda and 10 per cent higher than that given by Owen. It will be observed that with decrease in temperature from  $600^{\circ}$  K. down to the temperature of the room there is a more or less uniform increase of  $\chi$ . There then occurs a slight decrease in the susceptibility between room temperature and the temperature of solid CO<sub>2</sub>, after which the susceptibility shows an increase. The curve of  $I/\chi$  against T does not appear to call for special comment. It is obvious, however, that valuable information might be obtained at liquid-hydrogen temperatures, but these are beyond our present resources. The curve showing the variation of ferromagnetic correction with temperature is very striking, and there is no doubt whatever of the reality of the maximum there shown.

Specimen no. IV was prepared in the same way as no. IX except that the bulb A was accidentally cracked after the chromium had been powdered. The powder was placed in a tube, evacuated and heated to  $620^{\circ}$  C. for 4 hours, and then sealed. There was, therefore, the possibility that traces of oxygen and nitrogen might have had an opportunity of combining with the chromium, although precautions were

taken to evacuate the tube thoroughly before heating it. The curves of  $\chi$  and  $1/\chi$  are shown in figure 5 together with ferromagnetic corrections. There is some slight irregularity in the determinations, due mainly to uncertainty of correction for the ferromagnetic impurity, and it is seen that there is again a pronounced change in the paramagnetic properties as the temperature falls from that of the room to that of liquid oxygen, a change much like that found in specimen no. IX, except that there is now no sign of a decrease between + 14 and  $-78^{\circ}$  C. The value of the susceptibility  $3.86 \times 10^{-6}$  at room temperature (14° C.), was also rather high.

The preparation of specimen no. I differed from that of no. IX in that occluded gases were not so thoroughly removed. The curves corresponding to figure 3 obtained with this specimen were striking in that they were parallel within the limits of experimental error for temperatures between 350° C. and the room temperature, but the



Figure 5. Specimen no. IV. Maximum temperature during preparation,  $600 \,^{\circ}C$ . Graphs of  $\chi$ ,  $I/\chi$  and  $2\sigma$  as functions of temperature.

ferromagnetic correction assumed rather large proportions at temperatures below that of the room. This is shown by the ferromagnetic-correction curve of figure 6, where the variation of  $\chi$  and  $1/\chi$  with T for this specimen also are shown. The curve of  $\chi$  shows a much more pronounced rise than that which occurred in the case of specimen no. IX, and we satisfied ourselves with a copper-block experiment that the shape of the curve given in figure 6 is substantially correct. The  $1/\chi$  curve shows a very marked break in the neighbourhood of o° C. It provides a striking example of what is termed a *droite coudée*<sup>(6)</sup> or "elbowed curve", and we are tempted to enquire whether such curves really owe their existence to the presence of occluded gases in other experiments in which they have been recorded; we did not obtain such a marked break in any curve for specimens in which the hydrogen was effectively removed. The value of  $\chi$  at room temperature was  $3.80 \times 10^{-6}$ . The experiments so far described have been confined to specimens of chromium which have never been heated much above  $600^{\circ}$  C., and for such specimens we conclude that the most reliable value of the susceptibility at room temperature is  $3.2 \times 10^{-6}$  if they have never

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been in contact with air. It is interesting that we obtained about the same values as those obtained by Honda for our less pure specimens.

The peculiarities of figure 6 are attributed mainly to the effects of traces of mercury occluded in the chromium, which give rise to much uncertainty and irregularity in the determination of the ferromagnetic correction and to the pronounced upper sweep of the  $\{\chi, T\}$  curve with its associated elbow. From the other curves it appears clear that occluded hydrogen causes an increase in the value of the susceptibility, but its effect on the ferromagnetic correction could not be determined with certainty from the above experiments. The peculiar shape of the curves showing ferromagnetic correction against T was at first somewhat disturbing, but similar curves have previously been recorded by Ochsenfeld<sup>(7)</sup> for alloys of chromium with



Figure 6. Specimen no. I. Maximum temperature during preparation,  $420^{\circ}$  C. Graphs of  $\chi$ ,  $1/\chi$  and  $2\sigma$  as functions of temperature.

tellurium giving compounds  $Cr_3Te$ , CrTe, and  $CrTe_2$ ; these curves are reproduced in figure 7, and it is seen that a pronounced maximum occurs in the case of CrTe. It is unfortunate that Ochsenfeld did not extend his magnetic measurements to temperatures below that of the room. It may be suggested that as oxygen and tellurium are in the same column of the periodic table the ferromagnetism of our specimens may be due to traces of a compound of chromium and oxygen. We felt, however, that it is much more likely to be due to a combination of chromium with hydrogen and this view we think is supported by the experiments described in §5 below.

The effects of traces of mercury on the properties of chromium were brought out in the study of specimen no. III, which was not heated above  $370^{\circ}$  C. in the preliminary treatment. Starting at a temperature of  $-183^{\circ}$  C. and proceeding to  $350^{\circ}$  C., the susceptibility remained practically constant. Yet between  $320^{\circ}$  C. and  $350^{\circ}$  C. disturbances became apparent, the first results could not be repeated, and with decrease in temperature from  $350^{\circ}$  C. down to room temperature a constant

increase in susceptibility was recorded; below this the susceptibility somewhat decreased. In these measurements the ferromagnetic correction remained constant and small. The specimen was now heated to  $580^{\circ}$  C. with the empty end of the tube projecting beyond the furnace. A globule of mercury condensed in this end and was removed by sealing off and detaching a portion of the tube. Magnetic measurements were then reproducible, but the ferromagnetic correction, which was of the type shown in figures 4 and 5, was enormously increased; the maximum value of  $2\sigma$ , which occurred at approximately  $30^{\circ}$  C., was  $4.2 \times 10^{-2}$  per gram. Thus this



Figure 7. Ochsenfeld's curves showing variation of magnetization with temperature for compounds of chromium and tellurium.

specimen had associated with it a ferromagnetism at least twenty times as great as that obtained with specimen no. IX in the above experiments, as a result, no doubt, of the replacement of mercury by occluded hydrogen. It was therefore considered essential to evacuate the tube containing the specimen thoroughly during the hightemperature treatments described below, in order to remove all traces of hydrogen and mercury.

### §5. EXPERIMENTAL RESULTS FOR HIGH-TEMPERATURE PREPARATIONS

The material of specimen no. IX was placed in a quartz tube and kept at 800° C. for four hours while the tube was continuously evacuated. The tube was then sealed and allowed to cool slowly to room temperature, and the susceptibility of the material was then determined by the above method; absolute values were not found.

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The curve 1 of figure 8 shows the results obtained and there is no doubt that the ferromagnetic correction has enormously increased. The same tube was replaced in the furnace and maintained at a temperature of 1000° C. for two hours, further evacuation now being impossible. After cooling slowly the susceptibility was redetermined and curve 2 of figure 8 shows that the ferromagnetic correction had decreased to a remarkable extent; this decrease became even more marked when the specimen was heated to 1200° C. for about two hours, and curve 3 was found. The specimen now had the appearance of a sintered rod, and on breaking it up a bright grey powder—a pleasing contrast with our former black specimens—was obtained. The powder was placed in a pyrex glass tube, evacuated and heated to 450° C., and after it had been tempered for nine hours at 350° C., susceptibility measurements were made in the usual way. The relevant graphs of  $\chi_{\rm H}$  against 1/H are given in figure 9*a*.



Figure 8. Specimen no. IX after high-temperature treatment. Graphs of  $mg/H^2$ , which is a measure of susceptibility, as a function of 1/H, to show magnitude of ferromagnetic correction. Curve (1), after heating to 800° C. for four hours. Curve (2), after further heating to 1000° C. for two hours. Curve (3), after further heating to 1200° C. for two hours.

A most interesting feature of the behaviour of the specimen was that the ferromagnetic correction  $2\sigma$  was much smaller and practically constant within the limits of experimental error for all temperatures between  $-183^{\circ}$  C. and  $+350^{\circ}$  C., so that we feel justified in regarding it as due entirely to iron, presumably contained originally in the chromic sulphate and introduced by the electrolysis. It is commonly supposed that it is difficult to introduce iron into mercury, but that is not our experience; in any case the presence of iron to the extent of about two parts in one million of chromium would be sufficient to account for the results now described. It is considered that an X-ray examination of the material of no. IX before and after hightemperature treatment should be of interest, and this will shortly be undertaken.

The curve showing  $1/\chi$  against T, figure 9b, curve 2, indicates that over a range of temperature from about 35° C. to 350° C. the susceptibility obeys a Curie-Weiss relation of the form  $\chi = C/T + \Delta$ 



Figure 9*a*. Specimen no. IX after final high-temperature treatment. Graphs showing  $mg/H^2$ , which is a measure of susceptibility, as a function of r/H.



Figure 9b. Specimen no. IX. Final results after high-temperature treatment (at  $1200^{\circ}$  C.). Graphs of  $\chi$  and  $1/\chi$  as functions of temperature.

Below  $35^{\circ}$  C. the susceptibility shows a rather peculiar fall which may be due to a change in structure, or possibly to an imperfect correction for the ferromagnetism of the specimen, but the latter error is unlikely. Our final result is that susceptibility of the purest chromium so far obtained is  $3 \cdot 08 \times 10^{-6}$  e.m.u. per gram or  $160 \cdot 3 \times 10^{-6}$  per gram-atom at  $20^{\circ}$  C. uncorrected for diamagnetism of the core. The accuracy of this absolute value was limited by the accuracy with which the packing density could

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be found. To provide the usual basis of discussion, the final experimental values of  $\chi$  shown in figure 9*b*, curve 1, were corrected for the diamagnetism of the core of the chromium atom by the addition of  $0.127 \times 10^{-6}$  e.m.u. per gram<sup>(8)</sup>, and the reciprocals of these corrected values are given in curve 2 of figure 9*b*.

To facilitate discussion the treatment and properties of the several specimens are summarized in table 1.

Speci- men	Treatment	$\chi_{15}  imes 10^6$	Curve	Remarks	
I	Maximum temperature 400° C.	3.88	Fig. 6	Contained traces of mer- cury and hydrogen. Large ferromagnetic cor- rection of peculiar type (1)	
III	Maximum temperature 370° C.	(Not repro- ducible)		Ferromagnetic correction constant and small	
	Heated to 580° C. in eva- cuated sealed tube	4.78		Large ferromagnetic cor- rection with maximum at about 40° C.	
IV	Maximum temperature about 600° C.	3.86	Fig. 5 (Fig. 3)	Contained hydrogen. Fer- romagnetic correction with maximum value at about 40° C. type (2)	
IX	Maximum temperature about 600° C.; specimen completely prepared <i>in</i> vacuo	3.18	Fig. 4	Contained hydrogen only. Ferromagnetic correc- of type (2) with maxi- mum at about 60° C.	
	Specimen no. IX heated to 800° C. in evacuated quartz tube, and, after sealing, heated to 1200° C.; finally pow- dered, transferred to a pyrex tube, which was evacuated and sealed	3.00	Fig. 8, (Fig. 9 <i>a</i> and 9 <i>b</i> )	Free from hydrogen and mercury. Ferromagnetic correction small and constant over wide tem- perature range	

#### Table 1

#### §6. DISCUSSION OF RESULTS

The value of  $\Delta$  for chromium is considerably higher than that obtained by Bates and Reddi Pantulu for manganese. To some extent it is dependent on the value assumed for the diamagnetism of the atomic core, for if we take no account of this we find the Curie constant and  $\Delta$  to be respectively  $1.928 \times 10^{-2}$  and 5870. On the other hand, if we take the higher value  $17 \times 10^{-6}$  e.m.u. per gram-atom, assumed by Sommerfeld and Bethe<sup>(9)</sup> for the diamagnetism of the core, we find  $2.623 \times 10^{-2}$ and 7310 respectively. However, as the representation  $\chi = C/T + \Delta$  is purely formal, it need not be discussed further.

Now, it has been assumed in the above work that no changes occurred in the packing density of the specimen or in the area of cross section of the tube. Actually,

as the temperature of the specimen is raised the material must expand and the packing density be decreased. Disch<sup>(10)</sup> has measured the coefficient of linear expansion, of chromium over a wide range of temperature, and his results are given in table 2.

Temperature, T	- 78	100	200	300	400	500	° C.
Mean coefficient of expansion $\times 10^5$ , between 0° and T°	0.23	0.84	0.875	0.91	0.94	0.92	deg1

Т	a	Ы	le	2

From these figures we should expect the observed volume susceptibility to increase with fall in temperature and the increase to become more pronounced below o° C. However, Disch mentions the interesting point that while chromium contracts on cooling until the temperature reaches about  $-183^{\circ}$  C. it expands on further cooling to  $-190^{\circ}$  C. Thus while the contraction per metre between +20 and  $-183^{\circ}$  C. was 1.25 mm., that between +20 and  $-190^{\circ}$  C. was only 1.00 mm. Disch states that the latter values are not accurate, for the chromium surface became deformed at liquid-air temperatures and precise measurements by the Fizeau interference method were impossible. The expansion and magnetic data appear to be in close accord, except that the magnetic measurements indicate that the expansion on cooling begins before  $-183^{\circ}$  C. is reached.

The thermal expansion of chromium is also of interest in connexion with the special features of the curves of figures 4, 5 and 6, for it is concluded that the presence of hydrogen has a pronounced influence in the region where anomalous expansion is found. This is, of course, in agreement with the well-known influence of hydrogen on the magnetic properties of iron<sup>(II)</sup>. It may safely be assumed that the hydrogen makes possible an exchange interaction between the electrons responsible for the magnetic properties of chromium, and so accounts for the observed ferromagnetism and the increased paramagnetism of the specimen and its pronounced temperature changes.

The expansion makes somewhat uncertain the comparison of our experimental results with those expected on the theory of paramagnetism developed by Pauli <sup>(12)</sup> and by Frenkel<sup>(13)</sup>, and discussed by Sommerfeld and Bethe<sup>(8)</sup> and in considerable detail by Stoner<sup>(14)</sup>. This theory gives the following expression for  $(\chi_A)_e$ , the resultant paramagnetic susceptibility of the quasi-free electrons in one gram-atom of the metal when the temperature T is less than  $1 \cdot 157 \times 10^4 V_0$ ,

$$(\chi_A)_e = 32 \cdot \mathrm{I} (q/V_0) \left\{ \mathrm{I} - 6 \cdot \mathrm{II} \times \mathrm{I0}^{-9} \left( \frac{T}{V_0} \right)^2 \right\} \times \mathrm{I0}^{-6},$$

where q is the number of quasi-free electrons per atom and  $V_0$  is the width of the energy band, or the maximum electron energy in the completely degenerate state, expressed in equivalent volts. Neglecting the second term in the above expression and substituting  $(\chi_4)_e = 3 \cdot 20 \times 10^{-6} \times 52 \cdot 01$ , we find  $V_0/q = 0.2$  volt, while the value estimated by Sommerfeld and Bethe using other data is 0.34 volt. These values are too low, so that it may reasonably be assumed that several electron-energy bands

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overlap and thus make the effective number of energy states greater. For example, if it is assumed that five energy bands, corresponding to the five energy states of the d electrons overlap, then the calculated values of  $V_0$  become five times as great as those above. Or we may say that the density of states at the top of the Fermi distribution is much larger than it would be for free electrons, or that positive interchange interaction effects occur, or that both these factors are effective.

It is of interest to compare the temperature-variation required by the above theory with that found in our experiments. Thus we find  $\chi_4 = 3.198 \times 10^{-6} \times 52.0$ at 203° K. and  $3.008 \times 10^{-6} \times 52.0$  at  $610^{\circ}$  K., when no correction is applied for expansion but correction is applied for diamagnetism of the core. If we take the coefficients of linear expansion of chromium and pyrex to be 9.7 and  $3.0 \times 10^{-6}$  per degree respectively, then the value of the atomic susceptibility at the latter temperature when corrected for expansion is  $3.119 \times 10^{-6} \times 52.0$ . Hence

 $\Delta (\chi_A)/\Delta T = 0.0126 \times 10^{-6}$ .

The theoretical value is  $-32 \cdot I (q/V_0^3) = 6 \cdot II \times 10^{-9} \times 2T \times 10^{-6}$ , whence taking T = 450 approximately, q = 6 and  $V_0 = 1.2$  volts, we get the value  $0.000613 \times 10^{-6}$ . The experimental value is therefore some twenty times as great as the theoretical value, on the assumption that q=6. Lower values of q would give an approximate agreement, and, indeed, are possible, since it is only the electrons in unfilled (or partial) bands which contribute to the susceptibility. Moreover, the equation used above is based on the assumption that the energy-distribution of states of the a electrons in the unfilled band is of the same type as that for free electrons, and this may not be an adequate basis of discussion.

## §7. ACKNOWLEDGMENTS

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