The Magnetic Susceptibility of Chromium*

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The magnetic susceptibility of chromium has been measured from −195°C to 1440°C and is found to increase from 3.42×10^{-6} to approximately 4.30×10^{-6} emu per gram at the highest temperature. A transition is recorded in the region of 1400°C marked by a sharp increase in susceptibility and a temperature hysteresis.

INTRODUCTION

THE magnetic properties of the nonferromagnetic transition elements have recently been studied by several different theoretical approaches. Néel[1] and others[2,3] have suggested from a slight extension of the arguments of the Heisenberg theory that there should be a negative interaction between the *d*-shells of the nonferromagnetic transition elements, especially chromium and manganese. More recently, Zener[4] has proposed that the exchange interaction between the *d*-shells is negative for all transition elements and that ferromagnetism in Fe, Co, and Ni is the result of a parallel coupling of the *d*-shells via the conduction electrons. Thus, although Néel and Zener use considerably different models, they both arrive at the conclusion that the nonferromagnetic transition elements should be antiferromagnetic.

Pauling,[5,6] on the other hand, has proposed a theory wherein the *d*-electrons are used in bonding and thus give little or no contribution to the magnetic properties. In another approach by Mott and Jones[7] the *d*-electrons of the transition metals have been treated as a degenerate gas with a low degeneracy temperature. The decreasing magnetic susceptibility with temperature of such metals as platinum and palladium have been explained using this model. Stoner[8] and later Wohlfarth[9,10] have examined the band structure of some transition metals and alloys having still other types of susceptibility behavior. This varied picture has led us to study experimentally the magnetic properties of chromium; we have measured its magnetic susceptibility over the temperature range −195°C to 1440°C.

EXPERIMENTAL METHOD

The chromium was originally obtained by Armstrong[3] from Johnson, Matthey & Company, Ltd. It was in the form of electrolytic flakes and, according to the manufacturer, 99.9 percent pure. The results of the magnetic measurements indicated that a small ferromagnetic impurity was present.

All electrolytic chromium contains hydrogen and oxygen to some extent. Brenner, Burkhead, and Jennings[11] have indicated that, unless great care is taken, metallic chromium will absorb up to 0.8 percent by weight of oxygen and a smaller amount of hydrogen during the electrolytic process. By heating in vacuum to 1200°C it is possible to remove 99 percent of the hydrogen, but during this process the oxygen reacts with the metal to form chromic oxide.

Two of the specimens (*A* and *B*) were oven heated at 10^{-4} mm pressure in quartz tubes to 1300°C. The temperature was raised slowly over a two hour period, and it was left at the highest temperature about 20 minutes. After cooling, the tube was sealed off, thus enclosing the sample to be measured in a small evacuated quartz vial. The third sample (*C*) was heated with a torch for a short period of time in an attempt to reach a higher outgassing temperature. Each sample weighed about 500 mg.

The measurements were made by the body force method using a small torsion balance.[12] The instrument is used as a null device with an electrodynamic restoring force. At room temperature the error in measurement is ±1 percent, but at both higher and lower temperatures this error is increased to about ±2 percent. Temperatures were measured with a calibrated platinum-platinum 10 percent rhodium thermocouple. From other experiments it must be concluded that at the highest temperatures errors of 20°C can be expected. These errors are due to the non-uniform heating zone in the furnace, and the fact that the thermocouple cannot be placed in direct contact with the sample.

To reach temperatures in the region of 1400°C a small radiation shield type electric furnace was used. The heating element was two strands of No. 20 platinum—30 percent rhodium wire wound on an alundum tube. Four radiation shields spaced 2 mm apart surround the core, the two inner shields being 1-mil platinum foil. A small blower forced an air stream

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[2] L. F. Bates, *Modern Magnetism* (Cambridge University Press, London, 1948), second edition, p. 387.
[3] L. D. Armstrong, Can. J. Research **28**, 44 (1950).
[4] C. Zener, Phys. Rev. **81**, 440 (1951).
[5] L. Pauling, Phys. Rev. **54**, 899 (1938).
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[7] N. F. Mott and H. Jones, *Theory and Properties of Metals and Alloys* (Oxford University Press, London, 1936), first edition, p. 189.
[8] E. C. Stoner, Proc. Roy. Soc. (London) **A154**, 656 (1936).
[9] E. P. Wohlfarth, Phil. Mag. **40**, 1095 (1949).
[10] E. P. Wohlfarth, Proc. Roy. Soc. (London) **195**, 434 (1949).
[11] Brenner, Burkhead, and Jennings, J. Research Natl. Bur. Standards **40**, 31 (1948).
[12] T. R. McGuire and C. T. Lane, Rev. Sci. Instr. **20**, 489 (1949).

between the furnace and the magnet pole pieces to prevent any possible local heating of the pole surfaces.

Since the chromium was sealed in a quartz container, the magnetic susceptibility of a similar empty quartz vial was measured as a function of temperature. It was found that the susceptibility was constant to within 3 parts in 250 from −195°C to 1440°C. We therefore believe that no appreciable error was introduced by the container.

RESULTS

In Fig. 1 are shown the magnetic susceptibility data for three different samples of chromium, all of which were vacuum annealed as previously described. In all our measurements the specimens exhibited a slight ferromagnetic impurity. Using an Owen-Honda correction, $\chi_\infty = \chi_H - \sigma/H$, the corrected susceptibility can be obtained from the intercept at $1/H = 0$. For specimen B these corrected values are shown for the temperatures 25°, 50°, 98°, and 205°C in Fig. 1D. Measurements were also made at liquid nitrogen temperatures. Here the field dependence was slightly larger than at room temperature and gave a corrected susceptibility value of 3.42×10^{-6} emu/g. In general, the field dependence decreased slightly in a regular manner with temperature for the five temperatures where data were recorded.

There are two main features of the data: first, the gradual increase of the susceptibility from −195°C to 1400°C, and second, a transition marked by a noticeable increase in susceptibility at 1400°C. Associated with this transition is a temperature hysteresis. Below 1300°C the susceptibility follows the previous measurements in a reversible manner. After several runs had been made on specimen A, we found that there was a gradual increase in susceptibility over the whole temperature region as compared to the first or second set of data. This we attributed to the slow reaction of the chromium with the quartz after prolonged exposure at very high temperatures. Examination showed that the surface of the chromium was discolored and that the quartz vial had an etched appearance.

At the completion of the susceptibility measurements a chemical analysis of the chromium was made by Mrs. Marion Glickman of this laboratory. It was found that samples B and C, which were analyzed together, contained 1.2 percent Cr_2O_3. A sample of chromium which had never been heated to the high outgassing temperature contained less than 0.1 percent Cr_2O_3. Specimen A was not analyzed.

DISCUSSION

Bates and Baqi[13] have prepared metallic chromium from an amalgam and have measured its magnetic susceptibility over the temperature range −183°C to 350°C. The values they obtained are practically constant over this range and are 12 percent lower than

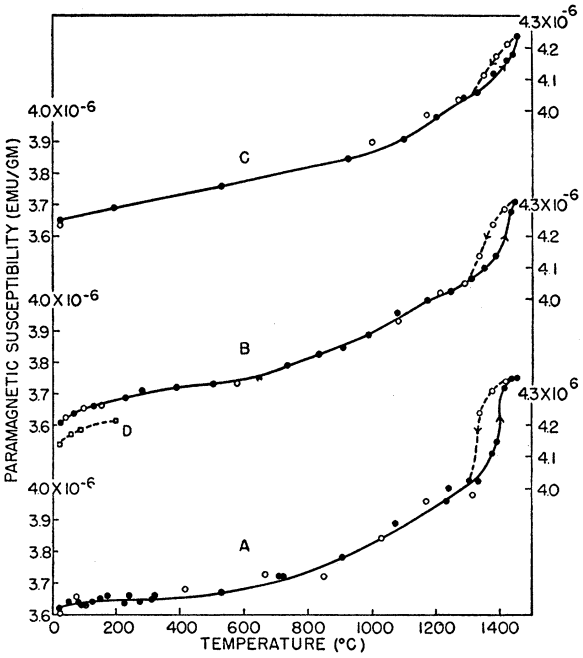

FIG. 1. The magnetic susceptibility of chromium as a function of temperature. A, B, and C are three different specimens with D showing ferromagnetic correction for specimen B.

ours. We believe that the higher susceptibility measured by us is a result of the presence of the Cr_2O_3 which was formed when our specimens were outgassed. Chromic oxide as an impurity in metallic chromium would not invalidate the observed temperature increase in susceptibility which we observed since the susceptibility of Cr_2O_3 decreases with temperature above 40°C.

Söchtig[14] has also measured the susceptibility of chromium, but only over a very small temperature range (16°C to 100°C with one value given at −183°C). His measurements from 16°C to 100°C appear almost independent of temperature and are in good agreement with our measurements. However, the value he reports at −183°C is 3.60×10^{-6} emu/g while our value is 3.42×10^{-6} emu/g.

The temperature increase of susceptibility of chromium, with the exception of the theory of Zener, is not in accord with existing theories of paramagnetic metals. For the most part past theories have limited their scope to temperature constant paramagnetism or to decreasing paramagnetism with temperature.

The theory of Zener postulates the presence of a negative exchange interaction in the transition metals making them antiferromagnetic. In antiferromagnetic substances the susceptibility increases with temperature until the Curie point is reached. Assuming a very high Curie temperature, Zener's theory could account for the increasing susceptibility which was observed in chromium over such a wide temperature range. Antiferromagnetic compounds also exhibit an increase of

[13] L. F. Bates and A. Baqi, Proc. Phys. Soc. (London) 48, 781 (1936).

[14] H. Söchtig, Ann. Physik 38, 97 (1940).

susceptibility with increasing field. If chromium were antiferromagnetic, one might expect to observe this effect. Our field dependence measurements, however, and those of other investigators indicate the opposite behavior, which is interpreted as a ferromagnetic impurity.

The excess specific heat found by Armstrong[3] has been suggested to be of antiferromagnetic origin. On the other hand, preliminary neutron diffraction work by Shull[15] does not seem to show any magnetic lattice such as that found in antiferromagnetic compounds. This latter result would seem to be strong evidence against chromium being antiferromagnetic.

Stoner[8] and also Wohlfarth[9] have treated, on the basis of the collective electron theory of ferromagnetism, the magnetic properties of various transition metals and alloys, extending the theory to an interpretation of paramagnetic susceptibility. Their discussions for chromium have applicability mainly to the susceptibility measurements of Bates and Baqi, which vary little with temperature. Chromium is qualitatively described as being similar to copper with a distribution of outer electrons having a small density of states and a high degeneracy temperature. Wohlfarth[16] points out that an increase in χ with temperature could be accounted for by a deviation of the band structure near the Fermi limit in the manner Stoner[8] has presented for barium. Such an approach awaits further theoretical investigation, for it it not clear what magnitude of susceptibility increase can be accounted for.

The rise in susceptibility and the resulting temperature hysteresis in the neighborhood of 1400°C is difficult to interpret. Although the shape of the susceptibility curve varies somewhat from sample to sample the increase of susceptibility at high temperatures is greater than the experimental error. We believe that there is a transition in the region of 1400°C in chromium marked by an increase in susceptibility of approximately 5 percent and accompanied by a temperature hysteresis covering a range of 50°.

The only other data on chromium which have been recorded over a wide temperature range are the electrical resistance measurements of Grube and Knabe,[17] who report a discontinuity in the temperature resistance curve. For different samples the discontinuity occurs at different temperatures ranging from 1350°C to 1540°C. The discontinuity is marked by a decrease in slope of the resistance curve. It was also found on lowering the temperature that a marked hysteresis takes place in some specimens. Grube and Knabe attributed the discontinuity and the associated hysteresis to the presence of chromic oxide, since they found that increasing the oxide content altered the temperature at which the anomaly occurred.

Since the resistance and magnetic anomalies occur in the same temperature region, we feel that they are due to the same cause. Also supporting this observation is the fact that temperature hysteresis is found in both types of measurements. The magnetic data, however, does not seem to verify the conclusion of Grube and Knabe that chromic oxide is the cause of the anomaly, for it is difficult to understand how the presence of Cr_2O_3 could account for the observed increase in susceptibility around 1400°C. Instead we believe that a transition occurs in chromium somewhere in the region of 1400°C to 1450°C which accounts for the sharp rise in susceptibility, and that the effect of the oxide is to vary the temperature at which the transition takes place. Another example of this ability of Cr_2O_3 to alter transition temperatures is found in the depression of the melting point of chromium due to its oxide content.

Anomalous behavior in chromium has been reported in electrical resistance[18] thermal expansion[19] and Young's modulus[20] at approximately 40°C. Our susceptibility measurements [Fig. 1A] and also those of Söchtig which were carefully made in this temperature region did not give evidence of a transition. There is, however, indication of a slight rise (about 2 percent) in the susceptibility measurements of Bates and Baqi in the neighborhood of 40°C. It is interesting to note that 40°C corresponds almost exactly to the antiferromagnetic Curie temperature of Cr_2O_3.

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[15] C. G. Shull, Phys. Rev. **82**, 771 (1951). *Note added in proof:*— Since this work was submitted, more recent results have been reported [C. G. Shull and M. K. Wilkinson, Bull. Am. Phys. Soc. **27**, 24 (1952)] indicating that chromium is weakly antiferromagnetic with an atomic moment of $0.40\mu B$ and a Curie temperature of 150°C.

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