crease of about 0.15a in Δa per defect in the colored specimens was expected, owing to the reduction in Coulomb repulsion, which would occur on trapping an electron at a negative-ion vacancy. This estimate is suggested by the observation that a 15 percent decrease in lattice dimension occurs when a chloride ion is replaced by a fluoride ion in KCl. The observed result could occur in such a case only if the concentration of F-centers were many times smaller than the concentration of Schottky defects.

ACKNOWLEDGMENT

The assistance of S. J. Marino in making the measurements is greatly appreciated.

PHYSICAL REVIEW VOLUME 98, NUMBER 4 MAY 15, 1955

Magnetic Susceptibility of Hafnium and Manganese

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(Received February 1, 1955)

The magnetic susceptibility of hafnium, which has been measured from 4.2°K to 1670°K, increases with increasing temperature above 77°K. At room temperature, the susceptibility is $(0.42\pm0.01)\times10^{-6}$ emu/g. The susceptibility of manganese between 77°K and room temperature shows a maximum at 125°K. This can be identified with antiferromagnetism by a correlation with neutron diffraction data. In the temperature region below 77°K the susceptibility increases again quite rapidly.

INTRODUCTION

THERE has been recent interest in the magnetic susceptibility of transition metals. On the basis of data recently obtained, Kriessman and Callen[1] have proposed a qualitative band theory interpretation of the temperature dependence of the susceptibility. We have extended this work by measuring the magnetic susceptibility of hafnium and manganese by the body-force method described in a previous paper.[2] The susceptibility of hafnium has not previously been measured while no data exist for manganese at low temperatures.

Manganese is of interest because Shull[3] has found evidence from neutron diffraction that it is antiferromagnetic with a Curie temperature at about 100°K. The only previous measurements on manganese in this temperature range are those of Serres.[4] They were limited to points at 80°K, 170°K, and room temperature, which gave some indication of a maximum in the susceptibility, an important characteristic of antiferromagnetism. It appeared that this feature needed further investigation to fix the exact location of the maximum value. No previous magnetic susceptibility data exist below 77°K, but it has been established by Goodman[5] using magnetic methods that manganese is not a superconductor down to 0.14°K. In all probability, Goodman's method would also have indicated a transition to ferromagnetism if it existed.

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[1] C. J. Kriessman, Revs. Modern Phys. **25**, 122 (1953); C. J. Kriessman and H. B. Callen, Phys. Rev. **94**, 837 (1954).
[2] T. R. McGuire and C. T. Lane, Rev. Sci. Instr. **20**, 489 (1949).
[3] C. G. Shull and M. K. Wilkinson, Revs. Modern Phys. **25**, 100 (1953).
[4] A. Serres, J. phys. radium **9**, 377 (1938).
[5] B. Goodman, Nature **167**, 111 (1951).

EXPERIMENTAL RESULTS

Hafnium

Our sample was obtained from H. K. Adenstedt of the Materials Laboratory, Air Materials Command, Wright-Patterson Air Force Base. Bommer[6] estimated from periodic table considerations that the susceptibility of hafnium should be about 0.5×10^{-6}. We find that the room-temperature value is $(0.42\pm0.01)\times10^{-6}$ and that the susceptibility increases regularly with temperature up to 1670°K, as shown in Fig. 1. The two upper curves (B and C) are from a series which one obtains from successive high-temperature runs. Curve A is the one finally reached, and, since it is reproducible and without field dependence, we assume it is the true behavior of the metal. The other curves evidently represent a ferromagnetic impurity whose effect slowly decreases on heat treatment. Measurements were also made at 77°K giving a value of 0.40

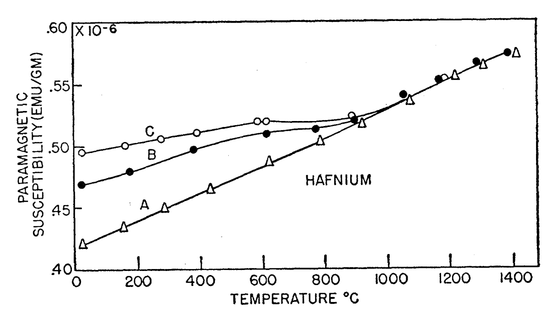

FIG. 1. Magnetic susceptibility of hafnium as a function of temperature. Upper curves (B and C) represent effects of ferromagnetic impurity.

[6] H. Bommer, Z. anorg. u. allgem. Chem. **247**, 249 (1941).

$\times 10^{-6}$ and at 4.2°K with a higher value of 0.46×10^{-6} emu/g.

Manganese

The sample of Mn came from Shull[3] and had been used in his neutron diffraction experiments. It had been heated by him in vacuo and then washed in acid. He gives its purity as 99.98 percent. The susceptibility measurements are illustrated in Fig. 2. There is a broad maximum at 125°K, and a large increase in susceptibility at liquid hydrogen and helium temperatures. This particular sample was analyzed by J. V. Gilfrich and E. D. Adams of the Naval Ordnance Laboratory for gas content, using vacuum fusion methods, with the following results: 0.00016 percent hydrogen, 0.0014 percent nitrogen, and 0.0011 percent oxygen by weight. The gas measured is from all sources, whether free or combined in chemical compounds such as MnO and MnO_2. It is believed that these quantities of gas are so small that they would not influence the susceptibility measurements.†

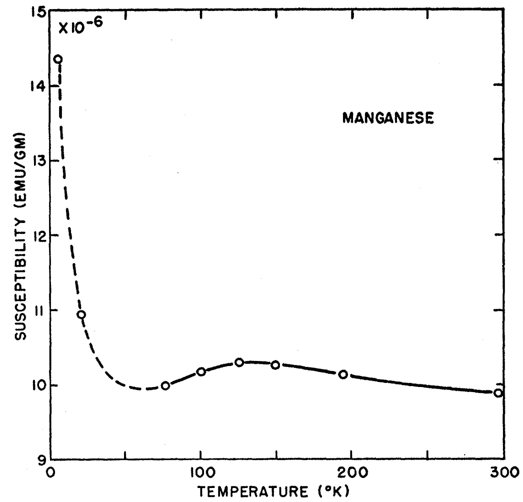

FIG. 2. Magnetic susceptibility of manganese as a function of temperature.

DISCUSSION

The behavior of hafnium is less complicated than that of manganese. The increase in susceptibility (χ) with temperature exhibited by this element is also found in other metals, such as tungsten, molybdenum[1] and chromium.[7] This temperature dependence can be qualitatively accounted for by the band theory of metals.[1,8,9] In general, the temperature coefficient depends critically on the shape of the density-of-states curve. An increase or decrease of χ with T depends on the position of the Fermi limit with respect to a maximum or minimum in the band form. Presumably, a more complicated temperature dependence of χ can be accounted for by assuming a more complicated band structure. The fact that the susceptibility of hafnium increases with temperature fits in with the band theory interpretation given by Kriessman and Callen,[1] which predicts that the temperature dependence of the susceptibility of the transition elements should be periodic with the columns in the periodic table.

The existence of ferromagnetic impurities that disappear with heat treatment as found in hafnium is not unusual. Evidently, iron impurities in uranium[7] have the same effect. It is believed that at the higher temperatures the ferromagnetic impurities are converted to paramagnetic compounds. If, now, this paramagnetism has a Curie law behavior, one would expect a slight increase to occur in the susceptibility at very low temperatures. Therefore, the increase in the χ of hafnium observed at 4.2°K might be due to this type of impurity.

The maximum in the susceptibility of manganese is almost certainly identified with antiferromagnetism. These measurements would place the Curie temperature at 125°K. Comparing the behavior of metallic manganese to antiferromagnetic compounds such as MnO and Cr_2O_3, one finds the same general features in the shape of the susceptibility curve. Shull[3] estimates the antiferromagnetic moment of the manganese atom as a few tenths of a Bohr magneton. With such a small moment, it is believed that the antiferromagnetism has only a small effect on the over-all susceptibility.

If the antiferromagnetism is ignored, then manganese shows a decreasing susceptibility from 4.2°K up to almost 1000°K, where a crystal structure transition occurs. This behavior is in qualitative agreement with the band theory treatment[1] mentioned above.

Palladium,[10] which also has a maximum at low temperatures, seems to exhibit the beginnings of a new susceptibility rise at 20°K, so that its over-all behavior may be analogous to that of manganese. There are also examples of antiferromagnetic compounds such as CoF_2 and NiF_2,[11] in which, below the Curie temperature, there is an increase in the susceptibility suggestive of the behavior of manganese.

ACKNOWLEDGMENTS

We wish to thank the personnel of the Cryogenics Section of the National Bureau of Standards for their cooperation in supplying the liquid helium used in this work.

† *Note added in proof.*—Recent work by Arrott, Coles, and Goldman indicates the low-temperature susceptibility of manganese may be very sensitive to small amounts of impurities, and that the increase below 77°K is due to impurities (private communication from J. E. Goldman, to be published).

[7] T. R. McGuire and C. J. Kriessman, Phys. Rev. **85**, 452 (1954) and **85**, 71 (1952).
[8] E. C. Stoner, Proc. Roy. Soc. (London) **A154**, 656 (1936); E. C. Stoner, Acta Metallurgica **2**, 259 (1954).
[9] E. P. Wohlfarth, Phil. Mag. **40**, 1095 (1949); Proc. Roy. Soc. (London) **A195**, 434 (1949).
[10] F. E. Hoare and J. C. Mathews, Proc. Roy. Soc. (London) **A212**, 137 (1952).
[11] W. J. deHaas and B. H. Schultz, Physica **6**, 481 (1939).