# 380. *The Magnetic Properties of Some Halides of Titanium and Zirconium.*

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The magnetic properties of some compounds of tervalent and bivalent titanium and zirconium have been measured in the temperature range 80—300° K. The ter- and bi-valent chlorides of titanium are antiferromagnetic with Neel points at 265° K and 85° K, respectively. The reasons for the very low moments, about 0·5 B.M., observed for the chloride, bromide, and iodide of zirconium(III) and the chloride of zirconium(II) are discussed. The anomalous behaviour of the susceptibility of titanium(III) chloride at low temperatures is also considered.

The temperature dependence of susceptibility of hexaureatitanium(III) perchlorate and sodium tetrachlorotitanate(II) is reported.

CERTAIN lower halides of titanium and zirconium are now more readily available pure. We have studied the magnetic properties of a number of compounds of ter- and bi-valent titanium and zirconium, and we discuss here the results of magnetic susceptibility measurements made in the temperature range 80—300° K. A summary of their magnetic properties is given in Table 1.

The magnetic properties of simple salts of the transition elements often differ radically from those of their co-ordination compounds, as in the latter group the paramagnetic ions are usually well shielded from neighbouring paramagnetic ions by diamagnetic ligand groups. In the simple salts, however, the paramagnetic ions often interact either directly, or through the agency of certain bridging diamagnetic ligands, *e.g.*, $O^{2-}$ or $F^-$, resulting in marked deviations of the properties of the metal ions from those of a simple gaseous ion which is considered in the majority of elementary theories.

The simple halides of tervalent titanium and zirconium offer a useful field for the investigation of these effects, particularly since the heavier transitional metals do not present any complication owing to intermediate coupling mechanisms, when the effect of spin-orbit coupling is being considered. Where appropriate we have also measured the temperature dependence of susceptibility of more magnetically dilute compounds in order to determine the effects of increased diamagnetic dilution on the properties of the various ions. It is convenient to divide the discussion on the basis of the *d* electron configuration of the metal ions.

TABLE 1.

Magnetic properties of halides of titanium and zirconium.

All values of $\mu_{eff}$ are calculated at 300° K from the relation: $\mu_{eff} = 2{\cdot}84\ (\chi_A\ T.)^{\frac{1}{2}}$; $T_N$ is the Neel temperature.

The compounds in parentheses were not studied in this work.

$d^1$ compounds

Simple halides:

TiCl$_3$ ... $\mu_{eff} = 1{\cdot}31$, $T_N = 165°$ K.

$$\left.\begin{array}{ll}(\mathrm{TiF_3})^{a} & \mu_{eff} = 1{\cdot}75 \\ (\mathrm{TiBr_3})^{b} & \mu_{eff} = 1{\cdot}38 \\ (\mathrm{TiI_3})^{b} & \mu_{eff} = 0{\cdot}87\end{array}\right\}\text{No evidence for antiferromagnetism.}$$

$$\left.\begin{array}{l}\mathrm{ZrCl_3} \\ \mathrm{ZrBr_3} \\ \mathrm{ZrI_3}\end{array}\right\}\ \mu_{eff} = \text{approx. } 0{\cdot}4.$$

Complex compounds:

[Ti$^{III}$ (urea)$_6$] (ClO$_4$)$_3$ .................... $\mu_{eff} = 1{\cdot}72$

Fused mixture of 3[Ph$_4$As]Cl + ZrCl$_3$ $\mu_{eff} = 0{\cdot}9$

$d^2$ compounds

TiCl$_2$ ... $\mu_{eff} = 1{\cdot}08$, $T_N = 85°$ K.

(TiBr$_2$)[c] $\mu_{eff} = 1{\cdot}26$.

(TiI$_2$)[c] $\mu_{eff} = 2{\cdot}09$ or $1{\cdot}05$, depending on structure.

ZrCl$_2$ ... $\mu_{eff} = 0{\cdot}6$.

Na$_2$TiCl$_4$ .................................... $\mu_{eff} = 2{\cdot}4$

[a] Ehrlich, *Angew. Chem.*, 1952, **64**, 617. [b] Klemm and Krose, *Z. anorg. Chem.*, 1947, **253**, 209. [c] Klemm and Grimm, *Z. anorg. Chem.*, 1943, **249**, 209.

## RESULTS AND DISCUSSION

d$^1$ *Compounds.*—There is some disagreement concerning the magnetic properties of titanium(III) chloride. Published measurements by Starr, Bitter, and Kaufmann[1] and Klemm and Krose[2] are compared with our results in Fig. 1. It must be pointed out that although the differences in absolute susceptibilities between the three sets of results are not large, there are important differences in detail and in the trends observed, *e.g.*, Klemm and Krose detect an antiferromagnetic transition at higher temperatures which is not observed by Starr *et al.* The increase in susceptibility at lower temperatures observed by Starr *et al.* is also of interest.

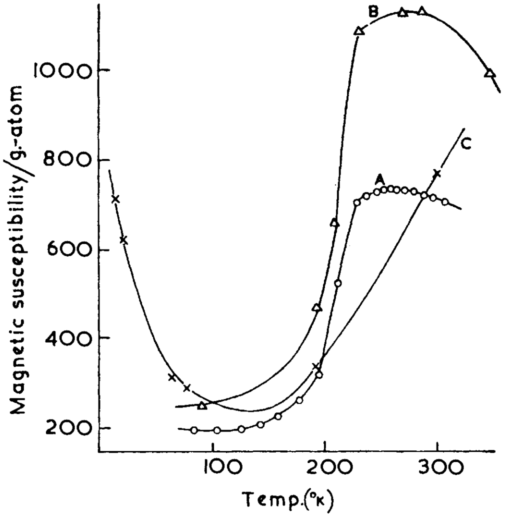

FIG. 1. Magnetic susceptibility per g.-atom against temperature for titanium(III) chloride. A, This work; B, Klemm and Krose; C, Starr, Bitter, and Kaufmann.

[*Added, March 29th,* 1962. The magnetic data for hexaureatitanium(III) perchlorate were fitted to the theoretical figures by using the free ion value of the spin-orbit coupling constant to obtain curve B in Fig. 2. It is more appropriate to use a reduced value $\lambda' = K\lambda$; in this way a better fit is obtained between theory and experiment, the values of $v$ and $k$ being 3·25 and 0·87, respectively.]

Both of the previous sets of measurements were made at relatively large temperature intervals so that the exact locations of changes of slope are uncertain; also the composition of the samples used was not reported. Our results have been obtained at much smaller

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[1] Starr, Bitter, and Kaufmann, *Phys. Rev.*, 1940, **58**, 977.

[2] Klemm and Krose, *Z. anorg. Chem.*, 1947, **253**, 209.

temperature intervals on carefully analysed samples. Our measurements are in agreement with those of Klemm and Krose in the high-temperature region, the susceptibility rising to a maximum at 265° K, which can be attributed to an antiferromagnetic interaction having a Neel temperature of 265° K. In the low-temperature region, Starr, Bitter, and Kaufmann report a broad minimum in the susceptibility plot at approximately 100° K; however, the small number of observations makes the position of this minimum uncertain. From the measurements reported here it would appear that a minimum may occur at about 80° K.

There are three possible explanations for the occurrence of this minimum: (i) the presence of a paramagnetic impurity, (ii) a phase change in the solid at low temperatures, or (iii) the presence of a ferromagnetic coupling in the lattice. The most likely impurities in titanium(III) chloride are titanium(IV) compounds, which would be diamagnetic, or less probably, titanium(II) chloride. Although we have shown that the susceptibility of titanium(II) chloride is very low and decreasing below 80° K, we cannot exclude the possibility that a " diluted " sample of titanium(II) chloride in titanium(III) chloride may not behave magnetically differently from the pure bivalent chloride.

Titanium(III) chloride exists in at least two forms at room temperature: a violet form and a brown form. The structure of the violet form is based on hexagonal close-packed chlorine layers, with titaniums in octahedral holes between every second layer of chlorine ions, the Ti–Ti distance being 3·6 Å in a layer, and 7·2 Å between layers.[3] The structure of the brown form has not been determined, nor has the effect of temperature on the structures been studied so that the possibility of a phase change cannot be ruled out.

We have measured the susceptibility of the brown form of titanium(III) chloride, and find that it is less than 200 c.g.s.u. $\times 10^{-6}$ per mole, considerably smaller than that of the violet form, and that there is no variation of the susceptibility with temperature within the limits of experimental error. At 80° K, the susceptibility is large enough to account for the flattening of the curve for the violet form in this region. No direct evidence of such a change from violet to brown form at low temperatures exists. Thus the possibility of this anomaly's being due to a phase change cannot be ruled out. Chemical evidence suggests that the brown form of titanium(III) chloride involves a high degree of local association which could explain its lower susceptibility.

Regarding the choice (iii), many compounds with layer structures are known in which ferromagnetic coupling occurs within a layer with an antiferromagnetic coupling between layers. Two cases are sufficient to illustrate this: (1) Both ferrous chloride and cobaltous chloride have been shown by Wilkinson, Cable, Wollan, and Koehler[4] to have this type of ordering; they also found that the ferromagnetic coupling is the stronger, despite the temperature dependence of susceptibility of these compounds being typical of an antiferromagnetic coupling together with some field dependence of susceptibility (cf. ref. 1). (2) In the case of CrSb, Lotgering and Gorter[5] have shown that the same type of ordering as in (1) occurs, again with a typical antiferromagnetic behaviour of the susceptibility. However, with CrTe–CrSb solid solutions, one being ferromagnetic and the other an antiferromagnetic alloy, a minimum in the susceptibility can be observed at low temperatures with a maximum at higher temperatures. However, the solid solution must contain at least 50% of the ferromagnetic alloy and also the susceptibility is markedly field-dependent. Since we have found that the susceptibility of titanium(III) chloride is practically independent of field strength in the range 3000—6000 oersteds, such arguments do not seem to provide an explanation in this case.

In general, titanium(III) salts do not behave in this manner, and as an example of magnetically dilute compounds of titanium(III), we report the temperature dependence of susceptibility of hexaureatitanium(III) perchlorate. These results are shown in Fig. 2.

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[3] Reed, University Microfilms (Ann Arbor), Publ. No. 21448. *Diss. Abs.*, 1957, **17**, 1479.

[4] Wilkinson, Cable, Wollan, and Koehler, *Phys. Rev.*, 1959, **113**, 497.

[5] Lotgering and Gorter, *Phys. and Chem. Solids*, 1957, **3**, 238.

The magnetic moment of this compound varies with temperature in the manner predicted by Figgis's theory[6] for the magnetic behaviour of an octahedral $d^1$ complex in which there is a trigonal or tetragonal distortion present. From Figgis's data, the experimental results can be correlated on the basis of $v = 3{\cdot}25$ and $K = 0{\cdot}8$, with some deviation from the theoretical behaviour at higher temperatures ($v = \Delta/\lambda$ where $\Delta$ is the trigonal distortion and $\lambda$ is the spin orbit coupling constant, and $K$ is a measure of the electron delocalisation). Theoretical and experimental data are compared in Fig. 2. This compound is thus a good example of a magnetically dilute titanium(III) compound, the moment being 1·72 B.M. at 300° K.

With the zirconium(III) salts, we find that the magnetic moments of the chloride bromide, and iodide are all very low (approximately 0·4 B.M. as compared with the expected value of 1·2 B.M. discussed below) which may be attributed to a strong antiferromagnetic interaction.

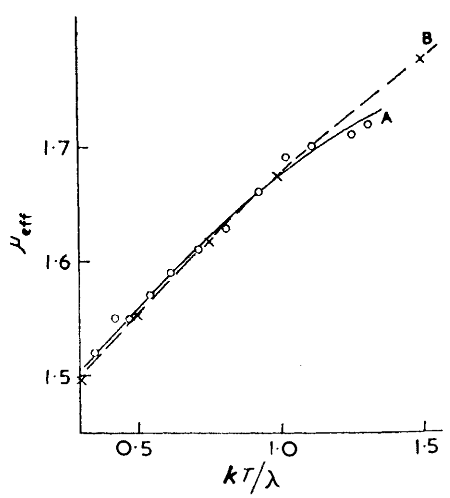

FIG. 2. Theoretical (B) and experimental (A) variation of effective moment with temperature ($kT/\lambda$), of hexaureatitanium(III) perchlorate.

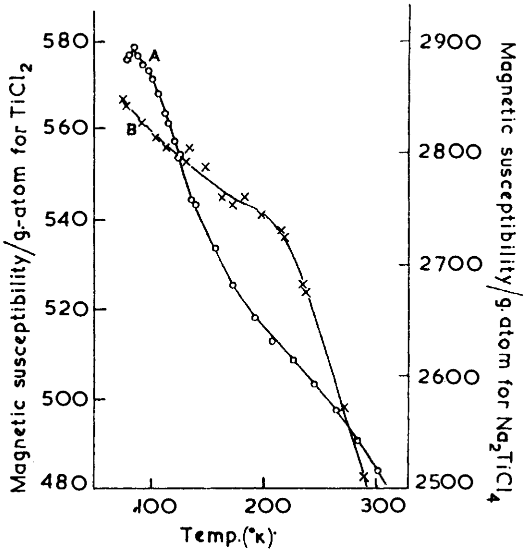

FIG. 3. Magnetic susceptibility per g.-atom against temperature for titanium(II) chloride and sodium tetrachlorotitanate(II). A, $TiCl_2$; B, $Na_2TiCl_4$.

The susceptibilities of samples of hafnium-free zirconium(III) chloride, bromide, and iodide are 70, 60, and 65 × $10^{-6}$ c.g.s.u./g.-atom, respectively, at 300° K, corresponding to effective moments of approximately 0·4 B.M. Two reasons for these very low moments can be postulated, either reduction of the moment due to spin-orbit coupling, or the presence of very strong antiferromagnetic interactions, including direct metal–metal bonding.

Using 500 as the free-ion value of the spin-orbit coupling constant, $\lambda$, for zirconium(III), Kotani's theory[7] predicts that the magnetic moment should be about 1·2 B.M. at 300° K, which is far in excess of the observed values, so that spin-orbit coupling mechanisms cannot completely account for the reduction in the moment observed. To test the alternative possibility of an antiferromagnetic exchange interaction, we have prepared a magnetically dilute complex of zirconium(III) chloride by treating it with fused tetraphenylarsonium chloride. The structure of the resulting complex is not known, but

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[6] Figgis, *Trans. Faraday Soc.*, 1961, **57**, 11, 198.

[7] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.

from the known composition of the melt, the calculated $\mu_{\text{eff}}$ for zirconium(III) ions in this magnetically dilute environment is 0·9 B.M. This is closer to the value predicted by Kotani's theory, and the increase in susceptibility favours our interpretation of the low moment of the pure zirconium(III) chloride as being due to antiferromagnetic interaction. It has not been possible to measure the temperature dependence of susceptibility of the simple halides, so that no more direct evidence is available to support our suggestion.

$d^2$ *Compounds*.—We have found that zirconium(II) chloride, like the zirconium(III) halides, has an exceptionally low susceptibility, the value being $150 \times 10^{-6}$ c.g.s.u./g.-atom at 300° K (*i.e.*, $\mu_{\text{eff}} = 0{\cdot}6$ B.M., cf. spin-only value of 2·8 B.M.). Identical arguments as were used in the case of zirconium(III) halides lead us to believe that this is due to a strong antiferromagnetic interaction within the zirconium(II) chloride lattice. Kotani's theory predicts a reduction to $\mu_{\text{eff}} = 2{\cdot}6$ B.M. only for zirconium(II). As support for these arguments we have shown that titanium(II) chloride is also antiferromagnetic. According to Starr, Bitter, and Kaufmann,[1] the molar susceptibility of titanium(II) chloride rises smoothly from $526 \times 10^{-6}$ c.g.s.u./g.-atom at 300° K to $2000 \times 10^{-6}$ c.g.s.u./g.-atom at 20° K. Our measurements at smaller temperature intervals are shown in Fig. 3. The maximum in the susceptibility may be attributed to an antiferromagnetic interaction with a Neel point at 85° K. The observed magnetic moment of only 1·08 B.M. at 300° K is therefore not surprising. We thus conclude that zirconium(II) chloride is probably also an antiferromagnetic species. It has not been possible to prepare any magnetically dilute zirconium(II) compounds.

The magnetic moment of the more magnetically dilute compound sodium tetrachlorotitanate(II) is 2·43 B.M. at 300° K, much closer to the expected spin-only value for a $d^2$ ion; in contrast with the low moment of titanium(II) chloride. The shape of the susceptibility against temperature curve for the tetrachlorotitanate(II) compound (Fig. 3) is rather unusual. The change in slope of the curve at low temperatures suggests that a phase change occurs, but comparison of $X$-ray powder diffraction patterns of the material at 300° K and 80° K does not support this idea. The reason for this change in slope is not clear at present.

TABLE 2.

Magnetic susceptibility measurements.

| $TiCl_3$ | | $TiCl_3$ | | Ti (urea)$_6$ $(ClO_4)_3$ | | $TiCl_2$ | | $TiCl_2$ | | $Na_2TiCl_4$ | | $Na_2TiCl_4$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $T$° (K) | $10^6\chi_{\text{Ti}}$ | $T$° (K) | $10^6\chi_{\text{Ti}}$ | $kT/\lambda$ | $\mu_{\text{eff}}$ | $T$° (K) | $10^6\chi_{\text{Ti}}$ | $T$° (K) | $10^6\chi_{\text{Ti}}$ | $T$° (K) | $10^6\chi_{\text{Ti}}$ | $T$° (K) | $10^6\chi_{\text{Ti}}$ |
| 308·6 | 706 | 237·8 | 719 | 1·313 | 1·72 | 301·7 | 484 | 121·1 | 558 | 291·5 | 2511 | 166·4 | 2761 |
| 296·7 | 715 | 229·5 | 705 | 1·260 | 1·71 | 282·8 | 490 | 115·2 | 562 | 291·2 | 2508 | 149·6 | 2786 |
| 289·7 | 722 | 211·7 | 526 | 1·108 | 1·70 | 264·0 | 497 | 112·1 | 564 | 272·0 | 2570 | 132·5 | 2802 |
| 280·4 | 727 | 193·9 | 320 | 1·032 | 1·69 | 245·3 | 503 | 106·6 | 568 | 253·9 | 2676 | 131·7 | 2791 |
| 271·6 | 733 | 176·8 | 265 | 0·929 | 1·66 | 227·0 | 509 | 101·0 | 571 | 236·2 | 2675 | 113·6 | 2867 |
| 265·2 | 735 | 159·2 | 229 | 0·818 | 1·63 | 207·9 | 513 | 97·3 | 574 | 235·9 | 2682 | 105·6 | 2816 |
| 265·1 | 734 | 142·0 | 208 | 0·715 | 1·61 | 191·2 | 518 | 92·7 | 575 | 218·4 | 2726 | 93·3 | 2827 |
| 258·9 | 734 | 125·5 | 198 | 0·617 | 1·59 | 173·0 | 525 | 87·1 | 577 | 218·0 | 2730 | 92·9 | 2829 |
| 252·9 | 733 | 103·8 | 195 | 0·546 | 1·57 | 156·8 | 534 | 85·5 | 579 | 200·3 | 2745 | 79·7 | 2845 |
| 247·5 | 728 | 82·3 | 196 | 0·474 | 1·55 | 139·2 | 544 | 80·3 | 577 | 182·9 | 2758 | 79·0 | 2843 |
| | | | | 0·422 | 1·55 | 137·0 | 544 | 79·8 | 576 | 175·2 | 2754 | | |
| | | | | 0·352 | 1·52 | 126·0 | 544 | | | | | | |

We thus find an interesting correlation between the magnetic properties of the chlorides of titanium(III) and zirconium(III), and of titanium(II) and zirconium(II):

$TiCl_3$ $\mu_{\text{eff}} = 1{\cdot}31$ B.M., $T_{\text{N}} = 265$° K     $TiCl_2$ $\mu_{\text{eff}} = 1{\cdot}08$ B.M., $T_{\text{N}} = 85$° K
$ZrCl_3$ $\mu_{\text{eff}} = 0{\cdot}4$ B.M.     $ZrCl_2$ $\mu_{\text{eff}} = 0{\cdot}6$ B.M.

If the isovalent compounds have similar structures the Neel temperatures of the zirconium chlorides should be higher than those of the corresponding titanium compounds, since the former have lower values of $\mu_{\text{eff}}$. If one reduces an antiferromagnetic interaction by isomorphous dilution with a diamagnetic species, the observed $\mu_{eff}$ increases with increasing dilution and the Neel temperature decreases ($\mu_{eff}$ tends towards the spin-only value); thus the above prediction is justifiable. Further, if the exchange interaction occurs directly between neighbouring metal atoms one would expect a greater orbital overlap and hence stronger interaction with the larger zirconium ions compared to the corresponding titanium ions.

When the crystal structures of these compounds are known, it may be possible to decide if a direct or a super-exchange mechanism gives rise to the observed antiferromagnetism. It will also be very interesting to study the magnetic properties of the corresponding hafnium halides, since we would expect them to be very similar to those of zirconium, owing to the similar sizes of zirconium and hafnium ions.

## EXPERIMENTAL

Magnetic susceptibilities were measured over the range 80—300° K, by using the Gouy apparatus described by Figgis and Nyholm.[8]

*Preparation of Compounds.*—Titanium(III) chloride was prepared by reduction with hydrogen of titanium(IV) chloride vapour at 900° C. It is a violet powder (Found: Ti, 30·7; Cl, 67·4. Calc. for $TiCl_3$: Ti, 31·1; Cl, 68·9%). Hexaureatitanium(III) perchlorate was prepared by Barbieri's[9] method [Found: Ti, 6·5; C, 10·0; N, 23·3; H, 3·5. Calc. for $Ti(urea)_6(ClO_4)_3$: Ti, 6·8; C, 10·2; N, 23·8; H, 3·4%]. Titanium(II) chloride was prepared by the New Jersey Zinc Company (Found: Ti, 34·3; Cl, 65·2. Calc. for $TiCl_2$: Ti, 34·5; Cl, 65·5%). Sodium tetrachlorotitanate(II) was prepared by E. I. duPont de Nemours by fusing together sodium chloride and titanium(II) chloride (Found: Na, 20·0; Ti, 59·7; Cl 18·6, Calc. for $Na_2TiCl_4$: Na, 20·3; Ti, 60·2; Cl, 18·6%). This analysis is inconclusive but we find that the *X*-ray powder photographs of the material do not contain any lines due to sodium chloride or titanium(II) chloride, establishing that a complex has been formed. The preparation and analysis of zirconium(III) chloride, bromide, and iodide have been described elsewhere (Newnham and Watts [10]). The zirconium(III) chloride–tetraphenylarsonium chloride complex was prepared by adding the zirconium chloride to fused tetraphenylarsonium chloride (1 : 3 molar ratio) in an atmosphere of argon. Zirconium (II) chloride was prepared by thermal disproportionation of the tervalent chloride, the purity of the resulting material being established by *X*-ray methods.

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[8] Figgis and Nyholm, *J.*, 1959, 331.
[9] Barbieri, *Atti. R. Accad. Sci. Torino*, 1915, **24**, 916.
[10] Newnham and Watts, *J. Amer. Chem. Soc.*, 1960, **82**, 2113.