

## Magnetic Susceptibility of Tetragonal Titanium Dioxide\*

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Careful measurements have been made of the magnetic susceptibility of the rutile and anatase crystalline forms of titanium dioxide. The magnetic susceptibility of a single crystal of high-purity rutile was found to be  $(0.067 \pm 0.0015) \times 10^{-6}$  emu per gram, and was temperature-independent from 55° to 372°K. Difficulty was encountered in obtaining a good value of the magnetic susceptibility of anatase because of impurities. However, a value of  $0.02 \times 10^{-6}$  emu per gram was obtained as a maximum value for anatase powder. A discussion is given for the different values obtained for anatase and rutile.

## INTRODUCTION

TITANIUM dioxide exists in three crystalline forms, tetragonal rutile and anatase, and orthorhombic brookite. Although many experimental values of the magnetic susceptibility of rutile have been reported in the literature, they exhibit considerable disagreement. The earlier results, which are listed in Table I, range from  $-0.3 \times 10^{-6}$  to  $0.37 \times 10^{-6}$  emu per gram. As far as we are aware, the only published determination of the magnetic susceptibility of anatase is the work of Zimens and Hedvall,<sup>1</sup> and no determination of the susceptibility of synthetic brookite has been reported.

TABLE I. Magnetic susceptibility of rutile.

Source	Temperature	Magnetic susceptibility ( $10^{-6}$ emu per gram)
Meyer <sup>a</sup>	288°K	0.37
Wedekind and Hausknecht <sup>b</sup>	room	0.066
Berkman and Zocher <sup>c</sup>	room	-0.20
Hüttig <sup>d</sup>	room	-0.30
Raychaudhuri and Sengupta <sup>e</sup>	...	0.073
Ehrlich <sup>f</sup>	90° and 293°K	0.08
Zimens and Hedvall <sup>g</sup>	...	0.134
Hill and Selwood <sup>h</sup>	k	-0.3
Reyerson and Honig <sup>i</sup>	301°K	0.061 <sup>1</sup>
Gray, McCain, and Masse <sup>j</sup>	room	0.075

<sup>a</sup> S. Meyer, Ann. Physik **69**, 236 (1899).<sup>b</sup> E. Wedekind and P. Hausknecht, Ber. deut. chem. Ges. **46**, 3763 (1913).<sup>c</sup> S. Berkman and H. Zocher, Z. physik. Chem. **124**, 322 (1926).<sup>d</sup> G. F. Hüttig, Z. anorg. u. allgem. Chem. **224**, 225 (1935).<sup>e</sup> D. P. Raychaudhuri and P. N. Sengupta, Indian J. Phys. **10**, 253 (1936).<sup>f</sup> P. Ehrlich, Z. Elektrochem. **45**, 362 (1939).<sup>g</sup> K. Zimens and J. Hedvall, Svensk Kem. Tidskr. **53**, 12 (1941).<sup>h</sup> F. N. Hill and P. W. Selwood, J. Am. Chem. Soc. **71**, 2522 (1949).<sup>i</sup> L. H. Reyerson and J. M. Honig, J. Am. Chem. Soc. **75**, 3920 (1953).<sup>j</sup> T. J. Gray, C. C. McCain and N. G. Masse, J. Phys. Chem. **63**, 472 (1959).<sup>k</sup> "Substantially independent of temperature," presumably down to -190°C.<sup>1</sup> The authors determined the magnetic susceptibility to be  $0.074 \times 10^{-6}$  emu per gram, but from their adsorption measurements they felt that  $0.061 \times 10^{-6}$  emu per gram would be more correct.

\* Publication authorized by the Directors of the U. S. Geological Survey and National Bureau of Standards.

<sup>1</sup> K. Zimens and J. Hedvall, Svensk Kem. Tidskr. **53**, 12 (1941).

This wide variation in the reported values, and the limited data available on the temperature dependence of the susceptibility, have induced us to undertake a more complete study of the purest obtainable rutile powder and single crystals. We have also made similar measurements on the purest obtainable powdered anatase. As no pure synthetic brookite could be obtained, no measurements could be made on this form of TiO<sub>2</sub>.

## EXPERIMENTAL METHOD

The magnetic susceptibility measurements were made by a modified Curie-Cheneveau method using a helical quartz spring balance (see Senftle *et al.*<sup>2</sup> and Thorpe and Senftle<sup>3</sup>).

A permanent magnet was allowed to descend slowly past the specimen, which was suspended from the end of a sensitive helical quartz spring. A microscope was used to measure the extension of the spring, and this extension was used to calculate the susceptibility.

The determination of the mass of the specimen was made by means of the same helical spring, after calibration with known masses. The size of a specimen was chosen so that the extension of the spring remained on the linear portion of the calibration curve. To check the operation of the balance, measurements were first made on standard specimens of platinum and of sugar (as described in reference 2).

Erratic behavior of the apparatus, arising from electrostatic effects, was corrected by silvering and grounding the inside of the glass envelope (with the exception of a small observation slit). Except for some of the oxygen adsorption tests at room temperature, all of the measurements were made in an atmosphere of helium, which provided thermal contact between the specimen and the coolant.

<sup>2</sup> F. E. Senftle, M. D. Lee, A. A. Monkewicz, J. W. Mayo, and T. Pankey, Rev. Sci. Instr. **29**, 429 (1958).<sup>3</sup> A. Thorpe and F. Senftle, Rev. Sci. Instr. **30**, 1006-1008 (1959).

Between 77 and 373°K, the temperature measurements were made with a chromel-alumel thermocouple and/or a conventional liquid thermometer. Below 77°K, a special gold-cobalt and silver-gold wire thermocouple was used. Although the thermocouple was placed close to the sample, it was not in contact with it, and hence the temperature data below 77°K may be in error by as much as three to four degrees. Above 77°K, the error in the measured temperature was much smaller than the experimental error in the magnetic susceptibility measurements.

To attain temperatures between 4.2 and 77°K, the inner Dewar flask was packed with charcoal and cooled with liquid helium. Above 35°K, the charcoal warmed up sufficiently slowly to obtain an adequate number of magnetic susceptibility measurements. However, between 4.2 and 35°K the warm-up time was so short that only a few measurements could be taken.

All results reported below have been corrected for the susceptibility of the balance pan and suspension. Above 10°K this correction was almost independent of temperature, but below 10°K it rose rapidly, so that at 4.2°K the correction was about  $0.3 \times 10^{-6}$  emu per gram, which was many times greater than the susceptibility of the specimen. The exact value of this correction was different for different runs depending upon contamination from the air and other sources, but may have been as high as 25–30% at 4.2°K.

#### PREPARATION OF SPECIMENS

##### Rutile

Two types of rutile were used in these experiments. Pure crystalline rutile from a boule and rutile powder were obtained from the Titanium Division, National Lead Company, South Amboy, New Jersey. Rutile

powder was also prepared by W. Brower of the Ferroelectricity Group, National Bureau of Standards. Spectrographic analyses of these materials are reported in Table II. The content of impurities, particularly of iron, was higher in the powdered rutile than in the rutile single crystal. The powdered rutile was found to have a surface area of 6 square meters per gram.

Both powder and single-crystal specimens were found to be extremely susceptible to contamination from the atmosphere—possibly ferromagnetic dust. This contamination was removed by soaking the specimens overnight in hydrochloric acid, followed by washing in cold water for one hour.

The powder specimens were compressed into pellets before susceptibility measurements were made. The direction of the crystallographic axis of an 8-mg single-crystal specimen of rutile was determined by x-ray diffraction. Within the experimental error the susceptibility was found to be the same in the *a* and *c* directions (as well as in a number of intermediate directions), so that the exact geometrical form of the specimen was of no importance. However, the shape of the specimen was irregular and approximately cubic.

##### Anatase

We were unable to obtain a single-crystal specimen of pure anatase. Consequently, all measurements were made using precipitated powder material. For this reason no experiments could be made to measure the susceptibility for different orientations in a magnetic field. Anatase was therefore assumed to be magnetically isotropic, just as rutile is.

Two sources of anatase were used, namely that produced by the Ferroelectricity Group, National Bureau of Standards (designated anatase No. 1), and

TABLE II. Spectrographic analyses of  $\text{TiO}_2$  samples. The figures in the table indicate the impurity content in weight percent.<sup>a</sup>

	(1) Rutile crystal <sup>b</sup>	(2) Rutile powder <sup>c</sup>	(3) Anatase (1) <sup>c</sup>	(4) Anatase (2) <sup>b</sup>	(5) Anatase (2) <sup>a</sup>
Silver	d	e	e	e	d
Aluminum	e	d	e	d	0.0005
Arsenic	d	d	d	d	d
Barium	e	0.001–0.01	0.0001–0.001	0.0001–0.001	d
Calcium	d	e	d	0.0001–0.001	d
Chromium	e	d	d	d	d
Copper	<0.0001	0.001–0.01	<0.0001	0.0001–0.001	0.0003
Iron	d	0.01–0.1	e	d	0.0027
Magnesium	0.0001–0.001	0.01–0.1	<0.0001	0.001–0.01	d
Manganese	d	0.0001–0.001	d	d	d
Nickel	d	e	d	d	d
Phosphorus	d	d	d	d	d
Lead	d	0.0001–0.001	d	d	d
Silicon	0.001–0.01	0.01–0.1	0.001–0.01	0.01–0.1	0.017
Tin	d	0.01–0.1	0.0001–0.001	0.001–0.01	0.0008
Titanium	>10	>10	>10	>10	>10
Vanadium	d	d	d	d	d
Tungsten	d	d	d	d	d

<sup>a</sup> All analyses by National Bureau of Standards except column (5) by National Lead Company.

<sup>b</sup> Rutile crystal and anatase (2) prepared by National Lead Company.

<sup>c</sup> Rutile powder and anatase (1) prepared by National Bureau of Standards.

<sup>d</sup> Not detected.

<sup>e</sup> Detection questionable.

that produced by the National Lead Company (designated anatase No. 2). The spectrographic analyses (see Table II) showed both samples to be reasonably pure, but in neither case was the impurity content as low as that of the single crystal of rutile.

The anatase prepared by the National Lead Company was calcined at 650°C for three hours to remove small traces of volatile impurity. Subsequent x-ray examination indicated that this high temperature converted three percent of the anatase to rutile. All measurements made on anatase No. 2 were therefore corrected for this small rutile content. Chemical analyses of specimens of anatase No. 2 indicated the presence of 0.8% water, 0.015% chlorine, 0.07% carbon dioxide, and 0.06% trivalent titanium, by weight. These analyses showed that the chlorine and the trivalent titanium were chiefly localized in the surface region of the particles.

Samples of 5–10 mg were used, and the powder was compacted gently, so that the measurements could be made on a geometrically stable solid, rather than on a loose powder. Microscopic examination did not show the powder to be "platy," and thus compaction could not induce any serious preferred orientation, even if the susceptibility were anisotropic.

Each sample compress was tested by plotting values of the susceptibility versus  $1/H$ , the reciprocal of the field strength, up to fields of 6000 gauss at liquid nitrogen and at room temperature. Unless the slope of the  $\chi_{(300^\circ\text{K})}$  versus  $1/H$  plot was zero, the corresponding specimen was rejected.

#### STOICHIOMETRY AND ADSORBED WATER

Ehrlich,<sup>4</sup> and Gray *et al.*<sup>5</sup> have shown that the magnetic susceptibility of rutile is increased by the presence of oxygen vacancies. For this reason precautions were taken to eliminate departures of the rutile samples from stoichiometry. When the specimens were heated in oxygen, no changes in weight or magnetic susceptibility were observed within the limits of the experimental error.

This result sets an upper limit of one part in  $10^4$ , by weight, to the oxygen deficiency. This deficiency would be expected to make a contribution of  $0.015 \times 10^{-6}$  emu per gram at 300°K to the (temperature-dependent) paramagnetic susceptibility. No such contribution to the susceptibility of rutile was observed. Hall measurements<sup>6</sup> on rutile specimens which had undergone various degrees of reduction also indicated that our unreduced crystals were stoichiometric to within one part in  $10^4$ .

Departures from stoichiometry are expected to introduce effects highly dependent on temperature, in contrast to the temperature-independent susceptibility of rutile reported in the next section. Gray *et al.*<sup>5</sup> have

shown that oxygen is only slightly adsorbed on unreduced rutile with no measurable effect on the susceptibility. They also report that the number of  $\text{Ti}^{3+}$  ions produced during reduction is not directly correlated with the amount of oxygen readsorbed and that at room temperature only about one-third of the oxygen is replaced.

Gray *et al.*<sup>5</sup> suggest that the low values of the susceptibility previously reported in the literature may be due to incomplete dehydration. They further show that water is very slowly desorbed from the surface of  $\text{TiO}_2$ , and that the significant change in the susceptibility could occur especially in powdered specimens. To circumvent this problem, we have been particularly careful to make our measurements on rutile specimens of low surface area, i.e., a fragment of a single crystal. The surface area of these specimens was smaller by a factor of about 100 000 than those of Gray *et al.*<sup>5</sup> for powdered specimens, and hence the effect of adsorbed water should be negligible. To check this, we have heated a specimen of rutile both to 900° in oxygen for  $1\frac{1}{2}$  hours and to 575°C for 7 hours in a vacuum, and found no measurable change in the susceptibility, mass, or color. A more severe treatment for a longer time in vacuum, as reported by Gray *et al.*,<sup>5</sup> will presumably remove water, but it was our experience that this procedure also removed oxygen from the lattice, causing a change in color from white to blue gray accompanied by a significant increase in the magnetic susceptibility.

The water content and concentration of trivalent titanium in our specimens of anatase No. 2 have been reported above, and are discussed further in a later section.

#### EXPERIMENTAL RESULTS

##### Rutile

To determine the temperature dependence of the magnetic susceptibility of rutile, a single crystal was preferred to powder specimens. In this way, the surface area was minimized so that the effects of the adsorption of gases and of contamination by dust were less important. In addition, the cleaning procedure was facilitated.

The experimental results are exhibited in Fig. 1. Above 55°K, no significant variation with temperature was found, and the mean of 44 determinations of the susceptibility of rutile was found to be  $(0.067 \pm 0.0015) \times 10^{-6}$  emu per gram. The measurement made at 4.2°K may be in error by as much as 25–30%. Because of the large increase in the susceptibility of the balance pan and suspension below 10°K, the value of  $0.12 \times 10^{-6}$  emu per gram of rutile at 4.2°K represents the difference between two comparatively large numbers, hence involves a larger percentage error.

With the foregoing reservation, the increase in the susceptibility of rutile at 4.2°K appears to be too great to be attributed to iron group impurities (see Table II). However, the temperature-dependent contribution

<sup>4</sup> P. Ehrlich, Z. Elektrochem. **45**, 362 (1939).

<sup>5</sup> T. J. Gray, C. C. McCain, and N. G. Masse, J. Phys. Chem. **63**, 472 (1959).

<sup>6</sup> H. P. R. Frederikse (private communication).

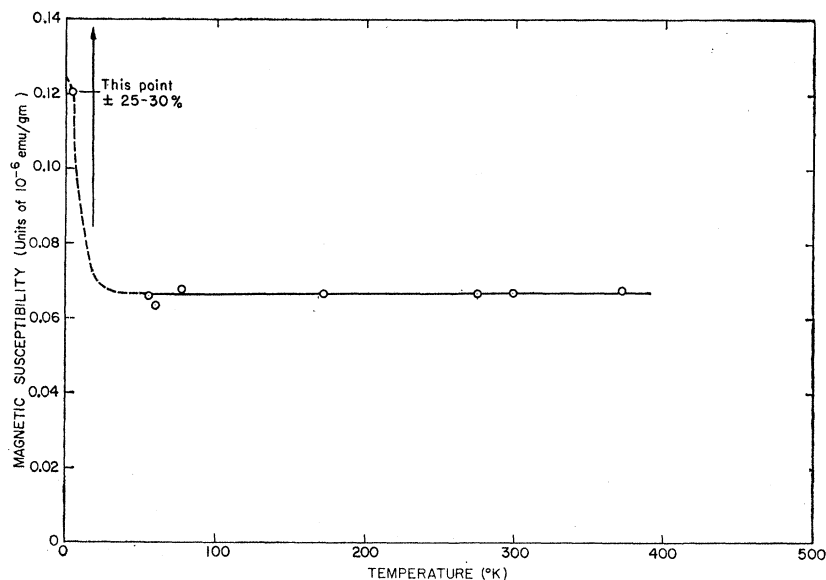


FIG. 1. Variation of the magnetic susceptibility of rutile with temperature.

( $0.12 \times 10^{-6}$  emu per gram at  $4.2^\circ\text{K}$ ) could arise if one titanium ion in about 30 000 were in the trivalent state. If all the  $\text{Ti}^{3+}$  sites arose from loss of oxygen, the corresponding weight loss would be one part in 75 000. This is below the limit of detection in our experimental determination of specimen weight gain when heated in an oxygen atmosphere.

Another possible source of this small, low-temperature anomaly is the presence of interstitial hydrogen atoms, arising from the preparation by the flame fusion method.

#### Anatase

Magnetic susceptibility measurements<sup>7</sup> were made on powder specimens in a helium atmosphere. In our earlier measurements the helium gas contained a small amount of oxygen impurity which readily adsorbed to the anatase powder. The susceptibility of the adsorbed oxygen caused a large increase in the susceptibility which reached a maximum in the vicinity of  $55^\circ\text{K}$ . A similar discontinuity has been reported by Onnes<sup>8</sup> in the susceptibility of oxygen at this temperature.

Using specially purified oxygen-free helium the measurements were repeated down to  $77^\circ\text{K}$ , and these are shown in Fig. 2. The helium cryostat was partially disassembled and data at temperatures lower than  $77^\circ\text{K}$  were not available for these later experiments.

All susceptibility measurements were found to be field-independent within the limits of the experimental error, at all temperatures, i.e., within one percent above  $77^\circ\text{K}$ , and within 2.5% below  $77^\circ\text{K}$ .

<sup>7</sup> As explained in an earlier section, the samples measured had been selected from a several-gram batch. Those samples were rejected which exhibited field-dependent susceptibility at room temperature.

<sup>8</sup> A. Perrier and H. Kamerlingh Onnes, Leiden Comm. No. 139c (1914).

#### DISCUSSION

According to a simple ionic model, the ions in the oxides  $\text{Sc}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{CrO}_3$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{CeO}_2$  possess noble gas configurations, hence would be expected to have a negative (diamagnetic) susceptibility. However, there is some evidence,<sup>9</sup> especially in the case of  $\text{V}_2\text{O}_5$ , for a contribution of temperature-independent paramagnetism larger than the negative (diamagnetic) term in the following equation<sup>10</sup>;

$$\chi_{\text{mol}} = - (Le^2/6mc^2) \sum \langle r^2 \rangle + (2L/3) \sum_{n' \neq n} \frac{|m^0(n':n)|^2}{h\nu^0(n':n)}. \quad (1)$$

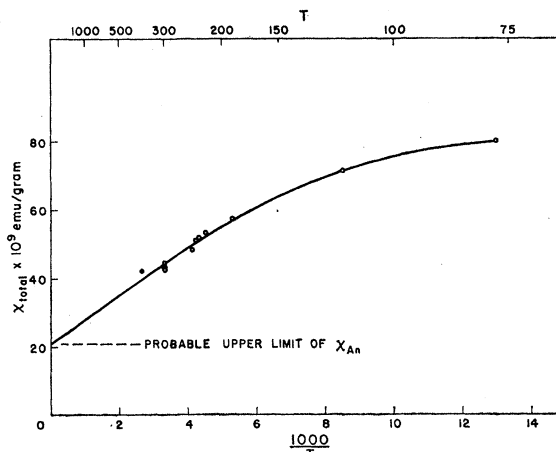


FIG. 2. Variation of the magnetic susceptibility of anatase powder. Data taken with oxygen-free helium as a transfer gas.

<sup>9</sup> W. Klemm and E. Hoschek, Z. anorg. u. allgem. Chem. **226**, 359 (1936).

<sup>10</sup> J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), p. 275.

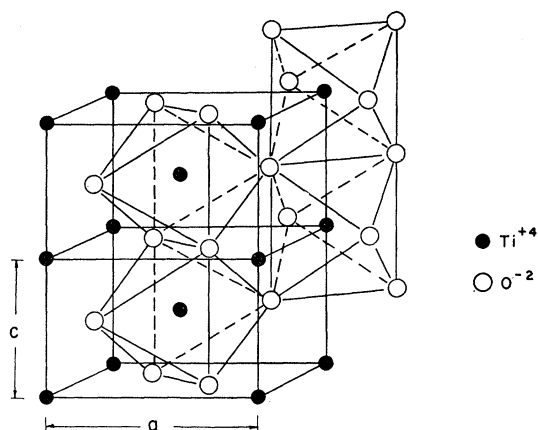


FIG. 3. Crystal structure of rutile:  $a=4.594$  Å,  $c=2.959$  Å,  $x=0.306$ . The titanium ions are at the positions  $(0,0,0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , and the four oxygen ions are at the positions  $\pm(x, x, 0)$  and  $\pm(\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2})$ .

In Eq. (1),  $m^0(n':n)$  is a nondiagonal element of the matrix for the magnetic moment operator evaluated in the unperturbed state of the system (i.e., in the absence of the magnetic field).  $\nu^0(n':n)$  is the frequency corresponding to the  $(n':n)$  transition. The indices  $n$  and  $n'$  refer, respectively, to the ground state and to an excited state of the system. The second term of Eq. (1) arises from states for which  $h\nu^0 \gg kT$ , i.e., those having a small Boltzmann factor.  $L$  is Avogadro's number,  $e$  is the electronic charge in esu,  $m$  is the electronic mass in grams, and  $c$  is the speed of light in cm/sec.  $\langle r^2 \rangle$  is the mean value of the square of the radius of an electron orbit summed over all the electrons.

### Rutile

The feeble temperature-independent paramagnetism exhibited by rutile in the range  $77^\circ$  to  $370^\circ\text{K}$  may well be explained by the assumption that the second term of Eq. (1) exceeds the first term in magnitude.

The unit cell of rutile is tetragonal, as illustrated in Fig. 3. The titanium ion is at the center of a distorted octahedron of oxygen ions. The Ti—O internuclear distances in the plane perpendicular to the  $c$  axis are slightly greater than the remaining Ti—O separations. The O—Ti—O bond angle which is bisected by the  $c$  axis passing through the titanium ion is only  $80.8^\circ$ .

We were surprised to find that the susceptibility was independent of the orientation of the crystallographic axis with respect to the direction of the magnetic field. The anisotropy of the dielectric constant of rutile would lead one to expect a dependence of the matrix elements of the magnetic moment vector on the crystallographic direction. In addition, the first term of Eq. (1) involves a type of averaging  $\langle \rho^2 \rangle$  replaced by  $(\frac{2}{3})\langle r^2 \rangle$  which assumes no preferred axis.

### Anatase

We expect the susceptibility of anatase also to be independent of temperature. However, our experimental results, plotted in Fig. 2, are highly temperature-dependent. We shall discuss the possibility of ascribing this temperature dependence to the presence of trivalent titanium sites, which have been detected by chemical analysis.

The effective magnetic moment of most iron group ions is a function of temperature. However, near room temperature it is usually a good approximation to use the "spin only" value, which, for  $\text{Ti}^{3+}$ , is 1.73 Bohr magnetons. The next approximation that we make is that the Curie law is valid for the  $\text{Ti}^{3+}$  ions in our specimens. With these approximations the total magnetic susceptibility,  $\chi_{\text{total}}$ , would be expected to depend on the temperature according to Eq. (2).

$$\chi_{\text{total}} = \chi_{\text{An}} + \beta^2 N / kT, \quad (2)$$

where  $\chi_{\text{An}}$  is the temperature-independent susceptibility of anatase, in emu per gram,  $\beta$  is the Bohr magneton,  $N$  is the concentration of  $\text{Ti}^{3+}$  sites per gram,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature.

Equation (2) describes a linear dependence of the total susceptibility on reciprocal temperature. The experimental curve, however, exhibits a decreasing slope for large values of  $1/T$  (i.e., low temperature). Such a decrease in slope is not unexpected. The calculations of Kotani<sup>11</sup> predict a decrease in the effective magnetic moment with lowering temperature for the case of a single  $d$  electron in a crystal field of perfect octahedral symmetry.<sup>12</sup>

In a crystal field of perfect octahedral symmetry, the fivefold degeneracy of the orbitals of a single  $3d$  electron (e.g., a  $\text{Ti}^{3+}$  ion) are split into an upper, doubly degenerate set, the  $d\gamma$  orbitals, and a lower, triply degenerate set, the  $d\epsilon$  orbitals. The energy difference between the  $d\epsilon$  and  $d\gamma$  orbitals is about  $20\,000\text{ cm}^{-1}$ , so that only the  $d\epsilon$  orbitals would normally be appreciably occupied. Under the combination of perturbations due to spin-orbit coupling and the distortion of the oxygen octahedra, a further splitting of the order of one to two hundred wave numbers is expected.

At temperatures such that  $kT$  is much greater than the over-all splitting of the  $d\epsilon$  orbitals, the square of the magnetic moment would be proportional to  $L(L+1) + 4S(S+1)$ , where  $L=1$ , i.e., the magnetic moment would include an orbital contribution. At sufficiently low temperatures (i.e.,  $kT$  much less than the separation between the ground state and the next higher state) the orbital contribution would become negligible.

The Kotani theory takes into account the effect of spin-orbit coupling, as a result of which there is no first-order Zeeman splitting of the ground state at  $0^\circ\text{K}$ .

<sup>11</sup> Masao Kotani, J. Phys. Soc. (Japan) 4, 293 (1949).

<sup>12</sup> A decrease in the intrinsic magnetic moment of the ferric ion in potassium ferricyanide at low temperature has been found by W. E. Henry, Phys. Rev. 106, 465 (1957).

On this basis one would expect the slope of the curve in Fig. 2 to tend to zero at low temperatures. However, the Kotani theory ignores the distortion of the  $d$  orbitals and the overlap onto the surrounding oxygen ions.

When account is taken of the overlap onto the ligands, and the departure from perfect octahedral symmetry, one obtains<sup>13</sup> again the possibility of a nonvanishing first-order Zeeman splitting at 0°K. The effective magnetic moment at 0°K would now be greater than zero but less than the "spin only" value of 1.73 Bohr magnetons. It is therefore reasonable to ascribe the decreasing slope in Fig. 2 to the reduction with falling temperature of the effective magnetic moment of a  $\text{Ti}^{3+}$  ion.

It can be seen from the foregoing remarks that an estimate of the contribution to the susceptibility arising from the measured concentration of trivalent titanium ions is best effected at room temperature, where the effective magnetic moment will be roughly 1.73 Bohr magnetons. Using the result of chemical analysis, 0.06% trivalent titanium ions by weight, a value of  $4.7 \times 10^{-6}$  is obtained for the coefficient of  $1/T$  in Eq. (2). The slope of the experimental curve, evaluated at room temperature, is  $7 \times 10^{-6}$ . The agreement is reasonably good when account is taken of the difficulties and uncertainties in the chemical analysis.

The intercept made by extrapolating the curve to  $1/T=0$  suggests that  $0.02 \times 10^{-6}$  emu per gram is a probable upper limit for  $\chi_{\text{An}}$ . This is considerably lower than the value obtained for rutile ( $0.067 \times 10^{-6}$  emu per gram). A small part of this difference may possibly arise from the water contained in the anatase specimens (0.8% by weight). Multiplication of this weight of water by Auer's value<sup>14</sup> of the diamagnetic susceptibility of water,  $-0.72 \times 10^{-6}$  emu per gram, yields a value of  $-0.006 \times 10^{-6}$  emu per gram for the possible contribution of the water. The remaining difference between the values for anatase and rutile evidently is associated with the different symmetries involved in the two cases. We have already discussed the symmetry of the titanium sites in the two materials (see Figs. 3 and 4). The difference in symmetry at the oxygen sites is even greater. Using the value for the diamagnetic susceptibility of the  $\text{O}^{2-}$  ion quoted by Selwood<sup>15</sup> ( $-12 \times 10^{-6}$  emu per mole), we would expect the

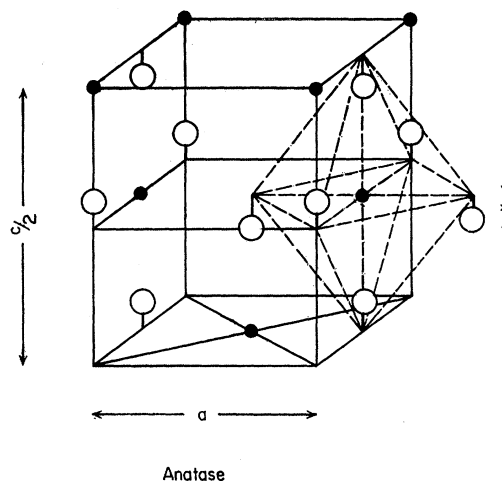


FIG. 4. Crystal structure of anatase:  $a=3.73$  Å,  $c=9.37$  Å,  $x=0.39$  Å.

oxygen ions to contribute about  $-0.3 \times 10^{-6}$  emu per gram to the susceptibility of anatase or rutile. The exact value of this contribution will depend somewhat on the symmetry at the oxygen site and may well explain much of the discrepancy. The diamagnetic susceptibility of the  $\text{Ti}^{4+}$  ion is  $-5 \times 10^{-6}$  emu per mole.<sup>14</sup>

It is not strictly correct to assume that this curve in Fig. 2 is linear at higher temperatures as expressed by the broken section. However, it is probably correct to assume that the intercept represents an upper limit to the magnetic susceptibility of stoichiometric anatase.

#### ACKNOWLEDGMENTS

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<sup>13</sup> W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.* **7**, 122 (1956).

<sup>14</sup> P. W. Selwood, *Magnetochemistry* (Interscience Publishers, Inc., New York, 1956), 2nd ed., p. 86.

<sup>15</sup> See reference 14, p. 78.