

MAGNETIC PROPERTIES OF THE ANATASE PHASE OF TiO<sub>2</sub>

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Magnetic susceptibility measurements of anatase single crystals of TiO<sub>2</sub> are reported for the first time. The anatase single crystals behave like a large gap semiconductor with a shallow donor level at 5 meV. The susceptibility measured by ESR is due to electrons localized on the donor state while the static susceptibility reveals the carriers thermally excited into the conduction band. The lattice contribution of the susceptibility is dominated by a net Van Vleck paramagnetism surprisingly lower in magnitude than in the rutile phase.

In the past, the electronic properties of TiO<sub>2</sub> have been extensively studied<sup>1-4</sup>. Among the three crystalline forms of TiO<sub>2</sub>, the rutile phase is the most widely investigated, mainly because of the ease in synthesizing large single crystals of this phase. The recent success in growing large single crystals of anatase<sup>5</sup> allowed the study of the bulk electronic properties of this low temperature phase of TiO<sub>2</sub>. Optical investigations<sup>6</sup> have shown that the band gap is slightly wider in anatase than in rutile. Photoluminescence studies are also reported<sup>7</sup> which show differences between the two phases. We have measured the transport properties (dc resistivity, Hall effect and thermopower) of as-grown anatase single crystals which behave like a wide band gap semiconductor with a very shallow donor level<sup>8</sup>. The n-type doping of anatase is due to oxygen off-stoichiometry. Surprisingly, the room temperature Hall mobility of the electrons is high in comparison with other transition metal oxides.

Here, we report both static and ESR magnetic susceptibility measurements of anatase single crystals. The ESR properties are due to a spin 1/2 carried by the neutral donors. The static susceptibility reveals the electrons excited into the conduction band. An important Van Vleck paramagnetism dominates the lattice diamagnetism.

The anatase crystals were grown by chemical transport reaction<sup>5</sup>. Both rutile and anatase crystals were produced in the same run during this process. The structure was checked by X-ray diffraction. Several crystals were investigated without significant difference in their transport and magnetic properties. The static susceptibility was measured with a Faraday balance in the 4-300 K temperature range. The ESR experiments were performed on a Bruker ESP300E spectrometer with a Helium gas flow cryostat at 9.4 GHz between 4K and 300 K. The changes in the Q value of the cavity due to the dielectric losses coming from the ionicity of anatase have been taken into account in the ESR susceptibility determination.

We have measured the resistivity and the Hall constant  $R_H$  as a function of temperature. The carrier density estimated from  $-1/eR_H$  is plotted on fig.1. The resistivity is plotted in the insert. Below 70 K, the carriers are electrons thermally activated from a donor level located at 70 K below the conduction band. Above 70 K, the exhaustion regime is reached. A rutile crystal grown in the same run is transparent, insulating ( $\rho \sim 10^7 \Omega\text{cm}$  at 300K), the Hall constant could not be measured: the rutile crystal is almost stoichiometric.

The static susceptibility of anatase and rutile is shown in fig.2. Above 100 K, a temperature independent value of  $0.5 \cdot 10^{-6}$  and  $5 \cdot 10^{-6}$  emu/mole is found, respectively. For the rutile sample where no ESR signal has been detected, the static susceptibility comes from the

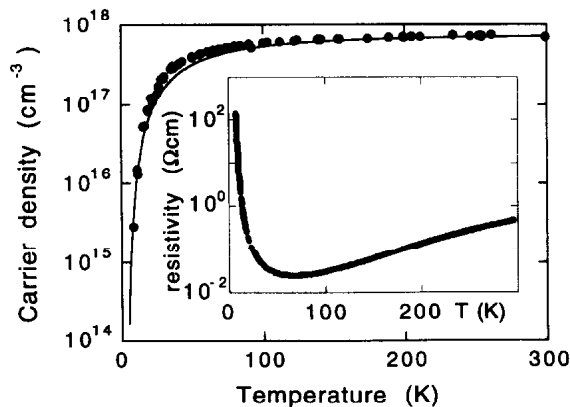


Fig.1: Carrier concentration versus temperature for an anatase crystal. The solid line is the fit with formula (1) of the text. The resistivity of the same sample is plotted in insert.

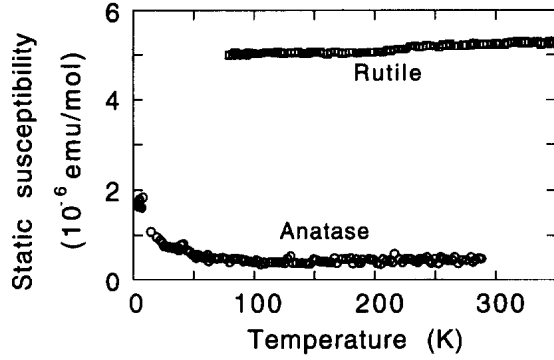


Fig.2: Static susceptibility  $\chi_s$  of anatase and rutile samples.

lattice contribution: core diamagnetism and Van Vleck paramagnetism. Calculating the core contribution from the Pascal constants, one gets  $-4 \cdot 10^{-5}$  emu/mole for TiO<sub>2</sub>. The susceptibility of the rutile sample is thus dominated by the Van Vleck contribution. This Van Vleck paramagnetism has already been pointed out by Keys and Mulay<sup>9</sup>. It increases with the oxygen understoichiometry. The value of  $5 \cdot 10^{-6}$  emu/mole is in agreement with the stoichiometric sample of ref.9 and corroborates the high resistivity of the sample.

Below 100 K, the temperature dependence of the susceptibility of anatase comes from localized spins. We have to evaluate this contribution in order to estimate the lattice susceptibility of anatase. This is the purpose of the ESR measurements.

A typical ESR pattern of the anatase crystals at 4.2 K is shown on fig. 3 (the magnetic field is along the [100] direction of the crystal). This pattern depends on the orientation of the magnetic field with respect to the crystal. It consists of three spectra labeled A, B, C on the figure. The ratio of the intensities are the following: B/A ~1% and C/A~0.1% for this sample. Depending on the sample, B/A varies between 0.5-3% while C/A remains around ~0.1%. We will focus on the A spectrum which is sample independent and gives the majority of the spin susceptibility. This spectrum comes from a spin 1/2. Its g tensor has the principal values 1.993, 1.986 and 1.968 for the principal directions [110], [1 $\bar{1}$ 0] and [001] of the crystal: these directions do not allow unambiguous identification of the center.

The temperature dependence of the ESR susceptibility is shown in fig.4. It is steeper than a Curie law. The equivalent Curie spins concentration estimated at 4.2 K is  $5 \cdot 10^{17}$  /cm<sup>3</sup>, a value which is comparable to the donor concentration. We will show that the ESR susceptibility comes from a spin 1/2 trapped on the neutral donor.

In order to model the electron/spin statistics, we will use a crude 2 level model based on the following assumptions. The donor level is located at  $-E_d$  below the conduction band which is assumed to be parabolic with an isotropic structure. The donor concentration is  $N_d$ . The conduction electron mass is taken to be the free electron mass  $m_e$ , following the results of ref. 6. The electrons activated from the valence band are neglected since the band gap (3.1 eV) is big compared with  $E_d$ . With these assumptions, the concentration of conduction electrons  $n$  and of neutral donors  $N_d^{\circ}$  is:

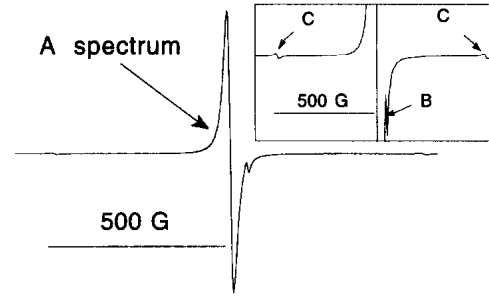


Fig.3: ESR pattern of an anatase sample at 4.2 K. The magnetic field is along the [100] axis.

$$n = \frac{1}{4} \left[ \sqrt{1 + \frac{8N_d}{N_c} \exp\left(-\frac{E_d}{k_B T}\right)} - 1 \right] \exp\left(\frac{E_d}{k_B T}\right) \quad (1)$$

$$N_d^{\circ} = \frac{N_d}{1 + \frac{1}{2} \exp\left(-\frac{E_d + E_f}{k_B T}\right)} \quad (2)$$

where  $E_f$  is the Fermi level position and  $N_c$  the effective density of states of the conduction band given by:

$$N_c = 2 \left( \frac{2\pi m_e k_B T}{h^2} \right)^{3/2} \quad (3)$$

By fitting the curve of fig.1 with formula (1), we found a donor level located 67 K below the conduction band with a donor concentration  $N_d = 7.7 \cdot 10^{17}$  /cm<sup>3</sup>.

Assuming that the neutral donors carry a  $S=1/2$  spins, the magnetic susceptibility of the neutral donors  $\chi_d^{\circ}$  is given by:

$$\chi_d^{\circ} = N_d^{\circ} \frac{g^2 \mu_B^2 s(s+1)}{3k_B T} \quad (4)$$

As shown in fig.4, this calculated susceptibility  $\chi_d^{\circ}$  is in good agreement with the ESR susceptibility suggesting that the A spectrum is due to an electron trapped on the neutral donor states.

When the temperature increases, these electrons are thermally activated into the conduction band contributing to a Pauli-like susceptibility  $\chi_c$ . It can be calculated by using:

$$\chi_c = -\mu_B^2 \int_0^{\infty} g(E) \frac{\partial f(E)}{\partial E} dE \quad (5)$$

where  $g(E)$  is the density of states of the conduction band and  $f(E)$  the Fermi-Dirac function. Within the 2 level model, it gives:

$$\chi_c = \frac{\mu_B^2}{k_B T} n \left( 1 - \frac{n}{2\sqrt{2} N_c} \right) \quad (6)$$

where  $n$  and  $N_c$  are given by formula (1) and (3).

This contribution is important above 150 K. We have not detected the conduction electron spin resonance, presumably because the line is too broad. However, this Pauli-like susceptibility enters into the static susceptibility measurement.

The total spin susceptibility is plotted in fig.5. The relative contributions are shown in the insert. We have also plotted the static susceptibility of the anatase sample shifted by  $-0.38 \cdot 10^{-6}$  emu/mole which results in a good

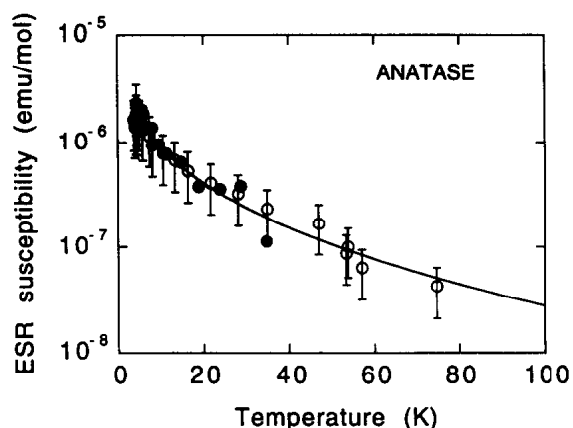


Fig.4: ESR susceptibility of two anatase samples. The susceptibility is due to the intensity of the  $\Lambda$  spectrum within 1%. The solid line is the calculated susceptibility  $\chi_{d^0}$  of one electron trapped on the unionized donor state (cf. formula 4).

matching of the 2 curves. This shift can be understood as subtracting the lattice contribution of  $0.38 \cdot 10^{-6}$  emu/mole from the static susceptibility. Assuming that the Van Vleck paramagnetism of anatase increases with the oxygen deficiency like in rutile<sup>9</sup>, it leads to a maximum Van Vleck contribution of  $+4.0 \cdot 10^{-5}$  emu/mole in anatase by comparison with  $+4.5 \cdot 10^{-5}$  emu/mole in stoichiometric rutile. This result is somewhat surprising. The Van Vleck contribution is related to the part of the orbital moment which is mixed into the spin ground state. This admixture is due to the low symmetry of the crystal field. Despite the lower symmetry of the anatase structure compared to the rutile, the Van Vleck contribution in anatase is smaller than in rutile. One possibility is that the symmetry of the crystal field is lowered in rutile by strong electron-phonon (polaronic) effects<sup>10</sup> which are weaker in anatase. The conduction electron mass values support this suggestion:  $m^* \sim 10\text{-}20 m_e$  in rutile while  $m^* \sim 1 m_e$  in anatase<sup>6</sup>.

In conclusion, the magnetic properties of as-grown (slightly understoichiometric) anatase have been measured for the first time and are in agreement with the transport properties. Both can be described within the framework of a two level scheme: a very shallow donor level located 67 K below the conduction band with a donor concentration

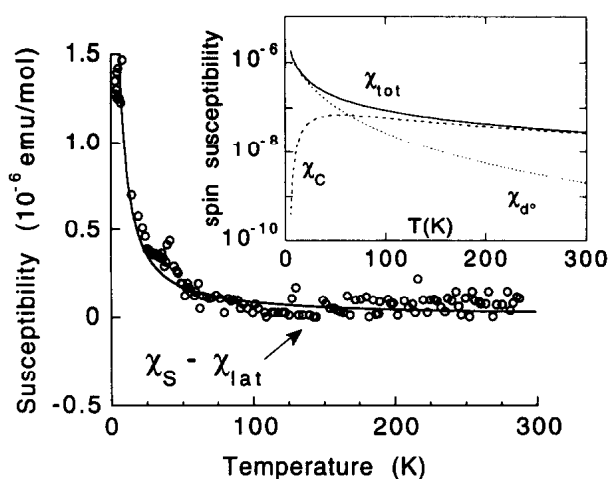


Fig. 5: Comparison between the calculated total spin susceptibility  $\chi_{tot}$  and the experimental static susceptibility  $\chi_s$  of anatase. A temperature independent lattice contribution  $\chi_{lat}$  of  $0.38 \cdot 10^{-6}$  emu/mole has been subtracted from the static measurement. As shown in the insert,  $\chi_{tot}$  arises from the electrons localized on the unionized donor level  $\chi_{d^0}$  and from the electrons activated into the conduction band  $\chi_c$ .

of  $7.7 \cdot 10^{17} / \text{cm}^3$ . The neutral donors carry trapped electrons whose spin dominates the ESR properties. When the trapped electron is excited into the conduction band, it contributes to the spin susceptibility with a Pauli-like susceptibility. The precise nature of the donor center is unknown at the moment.

The static susceptibility is dominated by Van Vleck paramagnetism above 100 K.

The differences observed between bulk rutile and anatase (shallow donor level, high mobility of the conduction electrons, smaller Van Vleck contribution) suggest that the polaronic effects are reduced in anatase by comparison with rutile.

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