

Magnetoelectricity in V_2O_3

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Motivated by the recent theoretical discussions on the implications of x-ray resonant scattering and linear dichroism data, we have measured the magnetoelectric effect in V_2O_3 . We were not able to detect any effect and could fix an upper limit for the magnetoelectric susceptibility $\alpha \leq 0.01$ ps/m. Moreover, we could verify that it is impossible to perform a magnetoelectric annealing on the system at the transition temperature, because of its small electrical resistivity. This finding has precise implications on the ground-state properties of the system.

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I. INTRODUCTION

In the last four years a rich harvest of data has become available regarding the phase diagram and the ground-state properties of V_2O_3 . The polarized neutron-scattering experiments by Bao *et al.*,^{1,2} the resonant x-ray scattering of Palasini *et al.*,^{3,4} the polarization-dependent $L_{2,3}$ -edge absorption data from Park *et al.*,⁵ and the κ -edge linear dichroism experiment performed by Goulon *et al.*⁶ give new insight on the system, contradicting the preexisting theories.⁷⁻⁹

Vanadium sesquioxide has long been considered to be the prototype of the Mott-Hubbard systems, after the intensive experimental and theoretical work of McWhan, Rice, and Remeika.^{10,11} In Ref. 11 three phases for the system are identified by varying the temperature and chromium doping: pure V_2O_3 at room temperature is a paramagnetic metal (PM); by decreasing the temperature a phase transition to an antiferromagnetic insulating (AFI) state is found at 150 K, while Cr doping ($\approx 1\%$) brings the PM state at room temperature to a paramagnetic insulating one (PI). The substitution of vanadium ions with chromium, enlarging the lattice parameters, can be considered as a negative pressure: because of this the PM-PI transition is of the kind predicted by Mott in his famous works.¹²

The magnetic order found by Moon¹³ in the AFI phase is very peculiar: it breaks the trigonal symmetry of the paramagnetic phases, as each V^{3+} ion is ferromagnetically coupled with one of the neighbors in the hexagonal plane and antiferromagnetically with the other two (see Fig. 1), even though the V_2O_3 lattice is not frustrated.

The widely accepted theory before 1999 was that of Castellani *et al.*,⁷ which was able to explain the anomalous magnetic order of V_2O_3 through the orbital ordering. The sign of the spin-exchange couplings depends on the orbital degrees of freedom and there exist some orbital patterns that allow the observed magnetic structure. But this theory was based on the assumption that only one of the two d electrons of the V^{3+} ion was magnetically active, the other being diamagnetically coupled in a molecular bond, thus giving an effective spin $S = \frac{1}{2}$ for each vanadium ion.

There is now definite evidence from the x-ray experiments^{3,5} that each vanadium ion carries a spin $S = 1$,

thus invalidating the old model. Because of this a lot of theoretical work appeared in the last three years,¹⁴⁻¹⁸ trying to explain the new experimental data available, but with very modest results, as shown in Ref. 18. One of the reasons, though not the only one, is the incapability of these models to explain the results of Ref. 6. We shall describe this problem more in detail, since the theoretical reasons that led us to perform our experiment are intimately linked to it.

In their paper Goulon *et al.*⁶ measured an x-ray linear dichroism in V_2O_3 , which was interpreted as a nonreciprocal effect and described by the time-reversal odd, real part of the complex gyrotropy tensor. A necessary consequence of this interpretation is that the system should be magnetoelectric (ME).¹⁹ Nonetheless, from x-ray crystallography^{11,20,21} and polarized neutron measurements,^{1,2,13} it is possible to infer that the magnetic space group of the system should be $C_{2h} \otimes \hat{\Theta}$, where C_{2h} is its classical space group and $\hat{\Theta}$ is the time-reversal operator.²² Because of the presence of the time-reversal symmetry and of an inversion center in the magnetic space symmetry group, V_2O_3 cannot be a magnetoelectric material.²³⁻²⁵ Moreover, a previous experiment²⁶ to detect the ME effect in V_2O_3 gave a negative result. Thus, either the x-ray linear dichroism experiment should be interpreted in a different way or there is a reduction of symmetry due to some degrees of freedom, other than the crystallographic position and the magnetic moments, that breaks both time-reversal and inversion symmetries. Note that both symmetries should be broken for a possible observation of the ME effect.

A physical possibility toward a reduction of the symmetry was suggested in Ref. 18, through the setup of an orbital order that breaks the inversion and time-reversal symmetries. But since none of the present theories (Refs. 14, 15, and 18) obtained such a ground state, this possibility is still controversial. Thus, the only way to check the validity of the interpretation given in Ref. 6, and also to obtain an argument to discriminate among the various theories, is to perform a direct measurement of the magnetoelectric effect on V_2O_3 . In this way we would be able to give independent information about the discrepancy between the magnetic space symmetry of this compound as detected by neutron¹³ and x-ray

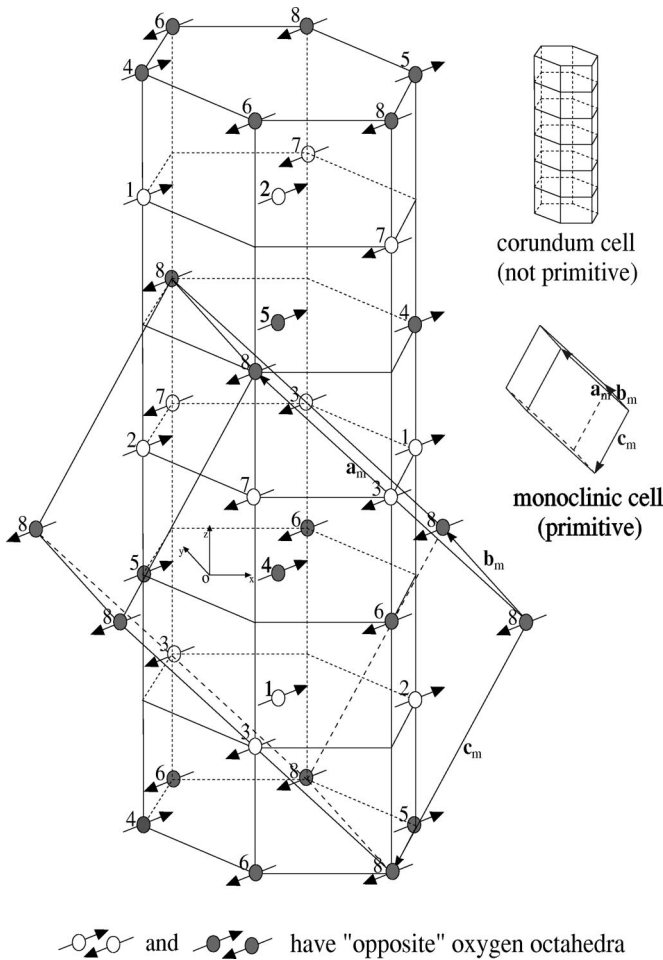


FIG. 1. Corundum and monoclinic cells for the paramagnetic and the antiferromagnetic phases of V_2O_3 , respectively. The distortion and increase in volume due to the monoclinic transition are not shown.

diffraction^{20,21} or by x-ray linear dichroism.⁶

There are only two subgroups of the magnetic space group $C_{2h} \otimes \hat{G}$ that allow a ME tensor different from zero:²⁵ the groups $2/m$ and $2/m$, in international notation. Other possible lower-symmetry groups, made by two elements, cannot explain the data of Paolasini *et al.*³ as shown in Conclusion. The ME tensors α relative to these two groups have different forms that allow their experimental determination. In a reference frame where the b_m axis is directed along the y direction, as in Fig. 1, the two tensors can be expressed as

$$\alpha_{2/m} \equiv \begin{pmatrix} 0 & \alpha_{xy} & 0 \\ \alpha_{yx} & 0 & \alpha_{yz} \\ 0 & \alpha_{zy} & 0 \end{pmatrix}; \quad \alpha_{2/m} \equiv \begin{pmatrix} \alpha_{xx} & 0 & \alpha_{xz} \\ 0 & \alpha_{yy} & 0 \\ \alpha_{zx} & 0 & \alpha_{zz} \end{pmatrix}.$$

II. EXPERIMENTAL SETUP

In order to mitigate the consequences of the destructive first-order phase transition,^{3,11} a Cr-doped sample was selected. The $(V_{1-x}Cr_x)_2O_3$ crystal used for the measurement ($x=2.8\%$) was a single crystal cut from the same specimen

as those used in Refs. 3 and 6. It was cubic shaped, with dimensions $2.20 \times 2.25 \times 2.50 \text{ mm}^3$, where the edges coincided, within less than 2° , with the hexagonal crystallographic axes $\langle 00.1 \rangle_H$, $\langle 11.0 \rangle_H$, and $\langle \bar{1}1.0 \rangle_H$. Electrodes were deposited by silver paint on the $\langle \bar{1}1.0 \rangle_H$ faces and then the sample was fixed to the sample holder by varnish.

The polarization of the sample was measured by a dc technique, where the current between the electrodes is measured and integrated by a Keithley 617 electrometer. The integrated value is scaled and displayed as a charge. In this way charges as low as 0.01 pC could be, in principle, detected. The measurements were performed in a superconductive magnet providing magnetic fields up to 10 T. The temperature was varied in a helium flow cryostat and measured by a calibrated Cernox resistance thermometer. The same experimental setup has been already used to detect the ME effect in the spin-flop phase of Cr_2O_3 .²⁷

We investigated only the presence of diagonal or off-diagonal components in the xy plane, so as to uniquely determine the symmetry of the ME tensor between the two shown above. The data were collected at two different temperatures (8 K and 14 K), in order to avoid accidental zeros of the magnetoelectric susceptibility.²⁸ Moreover, we searched for the ME effect at the lowest temperatures because the method of polarization measurements used needs a very high electrical resistivity of the sample (see Ref. 11 for the behavior of the resistivity vs temperature). At each temperature we performed a measurement with the magnetic field along the $\langle 11.0 \rangle_H$ direction and one along the $\langle \bar{1}1.0 \rangle_H$ direction. It is easy to demonstrate that in this way it is, in principle, possible to determine the nature of the ME tensor and, thus, of the magnetic space group, for any of the three monoclinic domain transitions.

After a first series of measurements without ME annealing, the whole procedure was repeated with ME annealing while cooling the system through the Néel temperature. For Cr_2O_3 , on which this procedure was first tested,^{29,30} the ME annealing is usually performed by cooling the sample through the transition temperature in a magnetic induction $B \approx 0.5 \div 1.5 \text{ T}$ and in an electric field $E \approx 5 \div 10 \text{ kV/cm}$. In this way it is possible to select one of the two ME domains by applying \vec{E} either parallel or antiparallel to \vec{B} . Which of the two domains is selected is nicely described in the paper by Brown *et al.*³¹ where the effect of simple magnetic annealing is also shown: while the ME annealing selects a full monodomain, magnetic annealing gives a sample domain unbalance between 30% and 80%.

III. RESULTS

The results for both procedures (with and without ME annealing) did not show any detectable polarization when the magnetic field was increased. In all the cases an exponentially decaying drift of the charge had to be subtracted, but we could easily check that it was a spurious effect, as it did not change when the magnetic field was stopped or, even, reversed. The origin of this decay is due to the coupling of the finite resistance of the sample ($R \approx 100 \text{ G}\Omega$ at 8 K) with

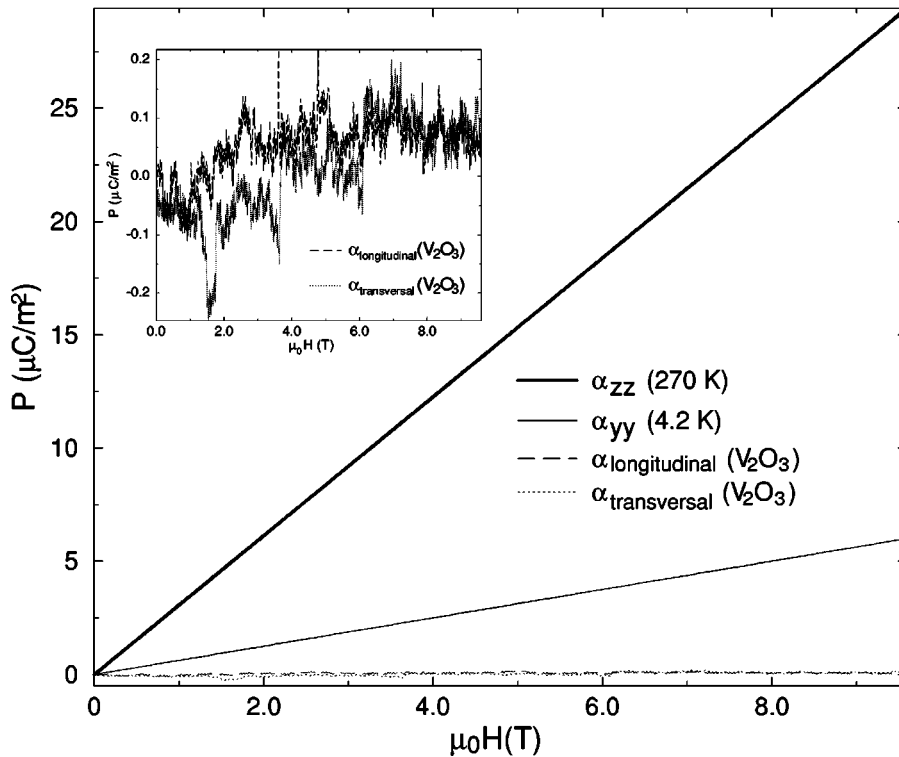


FIG. 2. The residual signal is shown, for both the longitudinal and the transversal cases, after ME annealing. It is compared with the case of Cr_2O_3 , as in Ref. 27, $P_z(H_z)$ (i.e., α_{zz}) and $P_y(H_y)$ (i.e., α_{yy}). The two lines are drawn just to give the order of magnitude, neglecting the changes due to the spin-flop transition above 6 T. In the window the residual signal is shown with an expanded scale.

the amplified capacitor of the electrometer ($C_E \approx 10$ nF) giving a time constant $\tau \approx 10^3$ s compatible with the measured one ($\tau_m = 1995 \pm 4$ s). Once this subtraction was done, we were left with a residual signal, shown in Fig. 2, whose analysis allowed us to determine an upper limit for the ME susceptibility: $\alpha \leq 0.01$ ps/m (3×10^{-6} in cgs units). This estimate was based on the angular coefficient of the linear fit of the residual signal shown in the window of Fig. 2. The result was $\alpha = 0.0097 \pm 0.0005$ ps/m. But at the same time the linear regression parameter r was $r = 0.54$, showing very poor agreement with a linear behavior, as expected by direct inspection of the figure. Moreover, since a similar drift was present also when the magnetic field was reversed, we believe that it was not linked to the ME susceptibility.

Just for the sake of comparison, in Fig. 2 are shown the polarization lines for Cr_2O_3 , corresponding to the longitudinal susceptibilities $\alpha_{zz}(270 \text{ K}) = 4.17$ ps/m (maximum signal) and $\alpha_{yy}(4.2 \text{ K}) = 0.8$ ps/m, as found in Ref. 27. The two lines are drawn multiplying these ME susceptibilities and the magnetic field.

There is another result to underline. While cooling and performing the ME annealing, we realized that this procedure could not work. The reason is that V_2O_3 is not a good insulator:¹¹ from the point of view of the conductivity, it can rather be classified as a semiconductor.^{32,33} The resistance of the sample at the transition temperature, in our experiment as in that of Ref. 6, was of the order of 10Ω . The application of an electric field of 5 kV/cm, through a capacitor, is equivalent to a voltage of 25 V at the surfaces of the sample. In such a situation the system can be better described as a conductor rather than as an insulator: the charges move in such a way as to make zero the electric field inside the sample. Consequently the local polarization generated by the external

electric field is reduced to zero. A quantitative estimate of the time required to the induced local polarization to decay to zero after the external electric field has been removed is simply given by³⁴ $t_R \approx \epsilon / \sigma$, where $\epsilon \equiv \epsilon_r \epsilon_0$ is the dielectric constant of the medium and σ its conductivity ($\sigma \approx 10^0 - 10^{-1} \Omega^{-1} \text{ m}^{-1}$). Estimating $\epsilon_r \approx 10$ we get $\epsilon \approx 10^{-10}$ F/m and $t_R \leq 10$ ns. This means that no local polarization can be present at the transition temperature, as the cooling process requires a much longer time.

Thus the whole procedure for V_2O_3 is no longer a ME annealing, but rather a simple magnetic annealing. The main difference with the case of Cr_2O_3 , where the ME annealing procedure works well, lies in the fact that the conductivity of Cr_2O_3 at its Néel temperature is more than 15 orders-of-magnitude less than that of V_2O_3 at its transition temperature.

IV. CONCLUSIONS

Even though the precision of the experiment should be improved to definitively rule out magnetoelectricity in V_2O_3 , we believe that important information can be extracted from our experiment, regarding the theories on the AFI phase of the system. The main point is related to the determination of the magnetic space group of the system. The absence of a ME signal, at our level of sensitivity, indicates that there is no reduction of the symmetry and the magnetic space group is still $C_{2h} \otimes \hat{\Theta}$. This is further confirmed by other indirect evidence coming from the vanadium K -edge scattering experiments of Paolasini *et al.*³ The interpretation of the $(221)_m$ reflection as a purely magnetic signal implies that the time-reversal symmetry associated to the body-centered translation is still an operation of the space magnetic group.

Moreover, the fact that at the $4p$ energy of the $(111)_m$ reflection no signal is detected is a clear indication that the glide plane symmetry still exists,¹⁸ associated with an inversion center, otherwise the structure factor would have given a signal different from zero.

It should be noted, also, that all the experiments performed in Grenoble (the present one and those of Refs. 3 and 6) used the same, Cr-doped crystal. This makes more straightforward the relative comparisons and shows that possible incompatibilities in the interpretations should not be attributed to the (low) Cr doping.

The last point to clarify regards the classification of V_2O_3 . Before 1970, because of the behavior of the resistivity,^{11,32} which ranges from $1\ \Omega\ \text{cm}$ to $100\ \Omega\ \text{cm}$, the PM-PI transition was called a metal-to-semiconductor transition.^{32,33} Only later, after the works of Rice, McWhan, and Remeika,^{9,11} was it recognized as a transition due to the strong correlations among the electrons, i.e., a Mott (or “metal-insulator”) transition. Nonetheless, not even in the AFI phase does the resistivity of V_2O_3 approach that of a

good insulator (at 100 K, for 2.8% Cr doping, $\rho \approx 0.5\ \text{M}\Omega\ \text{cm}$). In particular, at the transition temperature, the small value of the resistivity ($\approx 10^2\ \Omega\ \text{cm}$) does not allow the maintenance of an electric field inside the sample and the ME annealing procedure, contrary to the case of Cr_2O_3 , cannot be used for V_2O_3 .

In conclusion, we could not find any ME signal in V_2O_3 , in contradiction with the observation of a nonreciprocal x-ray linear dichroism⁶ and with the theoretical pictures that require symmetry-breaking orbital ordering.¹⁸ This calls for a different interpretation of the linear dichroism experiment that does not need a reduction of the symmetry and for further experimental investigations.

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