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Optical and magneto-optical study of orbital and spin ordering transitions in YVO_3

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Abstract

Optical and magneto-optical properties of YVO_3 single crystals have been studied in IR, visible, and UV regions. Below 74 K we have observed a large Kerr rotation, comparable to those in ferromagnets. This observation introduces a new class of materials: insulating antiferromagnets with strong magneto-optical Kerr effect, which can have advantages for practical applications. We look into the details of electronic and crystal structure changes. YVO_3 was found to undergo two structural phase transitions. Initially, the orthorhombic Pbnm symmetry is lowered below a second-order phase transition at 200 K and recovers below 74 K at a first-order phase transition. Two Mott–Hubbard (MH) bands dominate the electronic spectrum in the visible range, followed by charge-transfer gap in UV. Below the 200 K a transfer of the spectral weight to higher frequencies occurs and a third MH band appears at 3 eV. We discuss the results on the basis of spin and orbital ordering theory, proposed for YVO_3 . © 2002 Elsevier Science B.V. All rights reserved.

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YVO_3 is a canted antiferromagnet, where the net magnetic moment is formed by a small angle between the antiferromagnetically (AF) oriented spins of V^{3+} ions. As the temperature is decreased below 116 K, a small ferromagnetic moment appears. Upon further lowering the temperature, the magnetic moment gradually changes sign at around 90 K. This magnetization reversal was related to the mutually opposite effect of the Dzyaloshinsky–Moriya interaction and single-ion magnetic anisotropy in the direction of spin canting [1]. The magnetization switches sign again at 77 K. As the magnetic ordering changes from the C type to G type at this transition [2], the effect on magnetization was related to the orbital ordering on the vanadium sites [1].

The proposed picture lacks the microscopic understanding of the phenomenon. The aim of the present

research is to identify the electronic structure and its temperature variations. In this paper, we present optical and magneto-optical measurements of electronic excitations in YVO_3 single crystals. We compare the observed spectrum with our ligand field theory considerations and the LDA + U calculations.

The measurements were done using the ellipsometer technique in order to determine directly the real and imaginary parts of the dielectric function in the near-infrared, visible, and ultraviolet regions. The sample was placed in the ultra-high vacuum cryostat to avoid surface contamination at low temperatures. Samples with the a – b and b – c polished surfaces were used for the study. Crystal growth procedure is described elsewhere [1,3].

Room temperature YVO_3 has a distorted perovskite structure with the orthorhombic Pbnm crystal symmetry. The symmetry is lowered to triclinic, $\text{P}\bar{1}$, through the second-order phase transition, as we could judge from the phonon spectrum variations. The Pbnm symmetry is restored below the first order phase transition at 77 K [4].

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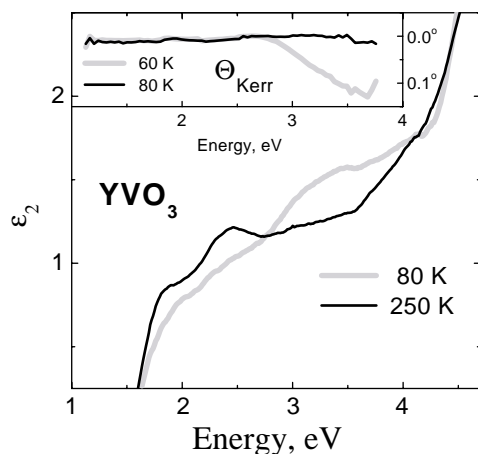


Fig. 1. Imaginary part of the dielectric function at 80 and 250 K. Inset: Kerr rotation above and below the first-order phase transition.

Fig. 1 shows the imaginary part of dielectric function measured at 80 and 250 K. YVO_3 is an insulator with the optical gap of approximately 1.6 eV and negligible conductivity below the gap. Three energy bands can be clearly resolved at low temperatures, with maxima being approximately at 1.9, 2.5, and 3.3 eV. We identify them with three Mott–Hubbard (MH) transitions, discussed below. The MH bands are followed by the charge-transfer gap around 4 eV. We restrict our discussion to the MH bands. The charge-transfer transitions have been studied previously [5].

There are two 3d electrons in the outer shell of the V^{3+} ions. In the strong crystal field approximation, the electrons occupy the lowest t_{2g} orbitals, which are further split due to Coulomb interaction into three energy levels, ${}^3T_{1g}$, ${}^1E_g + {}^1T_{2g}$, and ${}^1A_{1g}$. In agreement with the Hund's rule, the ground state is the ${}^3T_{1g}$ triplet. On-site d–d transitions are optically inactive due to effectively small distortions of VO_6 octahedra and are not considered. The MH excitations correspond to the transfer of electron from one vanadium site to another. In the final state, the first site has one d electron, which definitely occupy the only possible ${}^2T_{2g}$ orbital. The second site has three d electrons, which can form three energy levels, ${}^4A_{2g}$, ${}^2E_g + {}^2T_{1g}$, and ${}^2T_{2g}$. These are the three levels that we identify with the three bands observed in the experiment. Similar picture is obtained in LDA + U calculations. The calculations show that

the admixture of e_g orbital to t_{2g} is small and we indeed can exclude them from our consideration.

The temperature dependence of the MH bands is quite peculiar. With temperature being increased, two lowest bands gain strength, while the highest band loses intensity to the level of invisibility. A possible reason for this dependence can be an AF ordering or AF and orbital ordering. The latter was proposed for the electronic structure of YVO_3 , where the xy orbital is always occupied, while the xz and yz orbitals alternate in the C- or G-type structure depending on the type of AF ordering [1]. We found that both type of ordering predict a correct qualitative temperature behaviour for lowest and the highest bands, but they just give opposite temperature dependence for the middle band. This probably imply that the orbital order has a more complicated structure.

There is a clear change of the electronic structure at the first-order phase transition, which is better seen from the magneto-optical data, shown in Fig. 1. Below this transition we observed a manifold enhancement of the Kerr rotation. For the net magnetic moment as low as $0.01\mu_B$ per vanadium [1], the Kerr rotation reaches 0.1° .

In conclusion, we observed three optical bands in the electronic spectrum of YVO_3 , which we identified with MH transitions to ${}^4A_{2g}$, ${}^2E_g + {}^2T_{1g}$, and ${}^2T_{2g}$ levels of an V^{2+} ions. Similar electronic spectrum is obtained by LDA + U calculations. The bands reveal strong temperature dependence, which is still to be explained. There is an anomalous enhancement of Kerr rotation below the 77 K, which reflect the overall change of the magnetic symmetry at the phase transition.

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