Magnetic Field-Induced Shift of the Optical Band Gap in $Ni_3V_2O_8$

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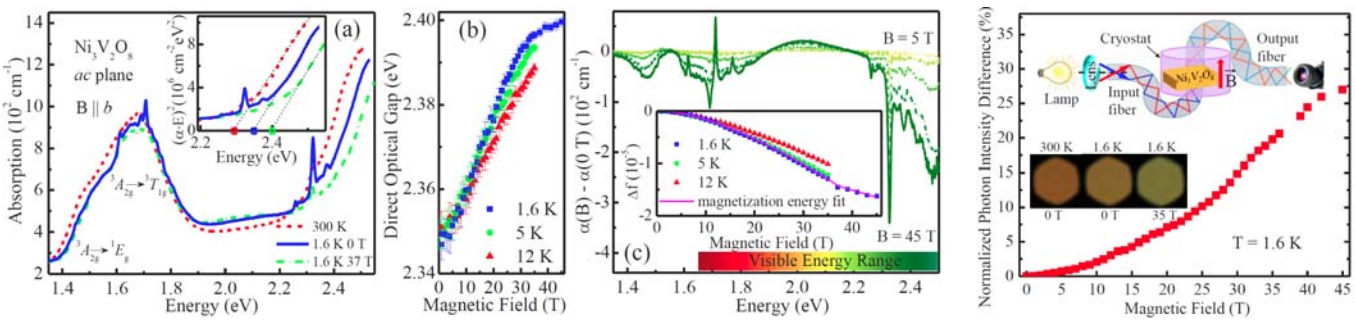
Introduction

The band gap is one of the most important electronic energy scales in a solid. It determines a variety of physical properties including *dc* resistivity, and it is vital to a number of applications like light harvesting. In both traditional semiconductors and complex oxides, the gap can be manipulated by chemical substitution, temperature, pressure, and electric field. Magnetic field also drives changes in the electronic properties. This effect can be as simple as the textbook case of Zeeman splitting of an isolated atom or as unexpected as amplified spin-charge interactions due to a collective phase transition in a solid. While field-induced band gap changes in conventional semiconductors are on the order of 0.1 - 0.3 meV/T, there are only a few examples of large shifts (on the order of 1 - 10 meV/T). Discovery of large magnetic field-induced changes in the optical properties requires reaching beyond traditional mechanisms like the Zeeman effect to include interactions that modify polarizability. Magnetic quantum critical transitions and their associated end points are rich places to search for amplified spin-charge interactions. Moreover, frustrated transition metal oxides are unrivaled in their ability to support competing interactions. Multiferroic $Ni_3V_2O_8$, with small exchange interactions, a frustration index > 5 due to the Kagome staircase structure, and a rich phase diagram with both plateaus and critical fields, is an attractive system with which to search for strong magnetoelectric coupling-induced effects.



Absorption spectrum of $Ni_3V_2O_8$ as a function of temperature and magnetic field along with gap determination; the direct optical band gap as a function of field; absorption difference spectra at various fields and a comparison of the change in oscillator strength to the magnetization energy; and photos of the color change process with temperature and magnetic field along with a schematic of our photography setup and an indication of the increased green color in magnetic field.

Results and Discussion

In this work, we report the discovery of a visible color change through the antiferromagnetic to fully polarized state transition in $Ni_3V_2O_8$. The 2.35 eV band gap blue shifts by 50 meV between 0 and the 37 T critical field (*B* || *b*) and saturates in the fully polarized state. This band gap shift makes $Ni_3V_2O_8$ more green from the spectroscopic point of view (24% at 45 T). We verify this picture with direct photographic images and discuss the transition in terms of coupling-induced modifications to the charge density. These findings reveal that key electronic energy scales like the charge gap can be tuned to a surprising extent with external stimuli, and that when major charge excitations appear in the visible range, field induced shifts can modify the color properties. What makes field so effective in this case is the presence of a collective transition in combination with strong dynamic magnetoelectric coupling. Other frustrated materials are likely to display energy transfer processes that mix magnetic quantum fluctuations and dielectric properties.

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