

Zeeman Effect of Cr^{3+} Fluorescence in SrTiO_3

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The purely electronic transition of the 8000-Å fluorescence of pure and chromium-doped SrTiO_3 has been studied using applied magnetic fields. The transverse Zeeman spectrum shows that the fluorescence is the magnetic dipole transition from the 2E_g to the ${}^4A_{2g}$ state of the Cr^{3+} ion. The 2E_g state is split by the tetragonal crystal field below 110°K. Relative intensities of the components with an applied magnetic field along a [110] direction show that the ν component lies highest in energy, indicating that the distortion is tensile.

SEVERAL recent reports¹⁻⁵ have discussed a fluorescent spectrum which appears in nominally pure and chromium-doped SrTiO_3 in the region of 8000 Å. The observed fluorescence consists of a zero-phonon line, a one- and two-phonon sideband spectrum, and for temperatures greater than 77°K a weak anti-Stokes spectrum. The zero-phonon line is observed to split into a doublet below the cubic-to-tetragonal phase transition at 107°K. This doublet is shown in Fig. 1(a) at 7°K.

Stokowski and Schawlow¹⁻³ have identified this spectrum as due to the 2E_g to ${}^4A_{2g}$ transition of the Cr^{3+} ion. This identification is based on the following observations. The zero-phonon line (the *R* line) splits into a doublet in the presence of the tetragonal field (below 107°K) and exhibits a Boltzmann factor between the components in fluorescence but not in absorption. The absorption is linear in chromium concentration and the excitation spectrum shows two pump bands, which is consistent with the behavior of Cr^{3+} in other materials. Other possible models have been proposed for this fluorescence. On the basis of photoluminescence and photoconductivity measurements Sihvonen⁴ has proposed that recombination to an unknown trapping center lying 1.58 eV below the conduction band is responsible for the infrared fluorescence. Grabner⁵ has proposed that the emitting defect is not Cr^{3+} but some other unknown defect. This argument is based on the fact that the *R* lines appear 1000 Å further into the red from the 4T_2 and 2T_1 bands than would be expected from crystal field considerations and on the fact that the behavior of the excitation spectra in the vicinity of the fundamental absorption edge differs from what would be expected for Cr^{3+} fluorescence.

In this paper, we present measurements of the transverse Zeeman spectra of the purely electronic transition of this fluorescence. These measurements show that the emission does arise from the 2E_g to ${}^4A_{2g}$ transition of the Cr^{3+} ion.

¹ S. E. Stokowski and A. L. Schawlow, *Bull. Am. Phys. Soc.* **11**, 886 (1966).

² S. E. Stokowski, Ph.D. thesis, Stanford University, 1968 (unpublished); *Phys. Rev.* **178**, 457 (1969); **178**, 464 (1969).

³ S. E. Stokowski and A. L. Schawlow, *Phys. Rev. Letters* **21**, 965 (1968).

⁴ Y. T. Sihvonen, *J. Appl. Phys.* **38**, 4431 (1967).

⁵ L. H. Grabner, *Bull. Am. Phys. Soc.* **13**, 1069 (1967); *Phys. Rev.* **177**, 1315 (1969).

The measurements were made at fields up to 26 kG in a superconducting coil with transverse access. The fluorescence was analyzed using sheet polarizer and measured with a 3.4-m Jarrell-Ash-Ebert spectrograph. The image plane of the spectrograph was scanned over a small distance with an S-20 photomultiplier tube. The spectrograph was equipped with a 7500-lines/in. Harrison grating blazed in 5.8 μ used in sixth instead of seventh order to obtain equal system efficiencies for both polarizations. A 500-W high-pressure mercury lamp with a CuSO_4 water filter and a Corning 4-94 glass filter was used to excite the fluorescence.

The samples were cut from boules grown by the National Lead Company. The data shown in Figs. 1 and 2 were taken on samples to which nominal con-

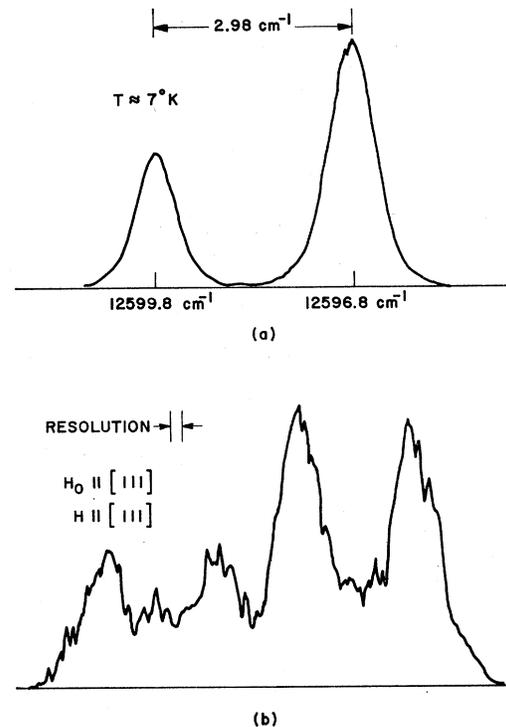


FIG. 1. (a) Spectrum of purely electronic line of the 8000-Å fluorescence. (b) Transverse Zeeman pattern of lines in (a) for $H_0 \parallel [111]$ and equal to 10 kG and $H \parallel [111]$.

centration of 0.005% Cr_2O_3 was added to the starting material.

The broad-band optical absorption spectra and spin-resonance properties of Cr^{3+} in SrTiO_3 have been investigated by Muller⁶ prior to the work discussed above. The Cr^{3+} ion was found to replace a Ti^{4+} ion with no local charge compensation. No fluorescence characteristic of the chromium ion was found. Low⁷ has reported the presence of axial sites due to a nearby charge compensator. The cubic Cr^{3+} site was found to exhibit a tetragonal distortion below 107°K consistent with the lattice phase transition at that temperature. The g factor for the $^4A_{2g}$ ground state was found to be 1.978.

The Zeeman effect of the Cr^{3+} R lines in various hosts has been previously studied. In particular, Sugano *et al.*⁸ have measured the longitudinal and transverse Zeeman spectra for Cr^{3+} at a cubic site in MgO and calculated the intensities of the relative components on a model of magnetic dipole transitions with spin-orbit coupling of the 2E_g and $^4T_{2g}$ electronic states. Imbusch *et al.*⁹ have extended these calculations to the case of tetragonal sites in MgO . Their results show that in that case the R -line transition is a mixture of magnetic and electric dipole components. The electric dipole component arises from the fact that a charge-compensating Mg vacancy along a $[100]$ axis lifts the inversion symmetry at the Cr site in addition to splitting the 2E_g state.

Figure 1(a) shows the purely electronic line at 7°K split 2.97 cm^{-1} by the tetragonal distortion of the lattice. At other temperatures the splitting Δ has a dependence on temperature of $\Delta \propto (T_c - T)^{1/2}$, where $T_c = 107^\circ\text{K}$ is the temperature of the cubic to tetragonal phase transition. This power dependence of the splitting on temperature is characteristic of a second-order phase transition. The data shown were taken at an average sample temperature of 7°K due to heating of the sample by the exciting light. Reduction of the pump light by a factor of 50–100 was required to bring the samples to bath temperature. Boltzmann distribution between the levels could then be observed as the bath temperature was varied.

Figure 1(b) shows the transverse Zeeman pattern with $H_0 \parallel [111]$ and equal to 10 kG and with the magnetic dipole vector $H \parallel [111]$. Figure 2 shows the experimental and the theoretical magnetic dipole intensities of the components of the transverse Zeeman patterns as a function of the direction of the applied magnetic field and the magnetic dipole vector. The theoretical intensities for $H_0 \parallel [001]$ and $H_0 \parallel [111]$

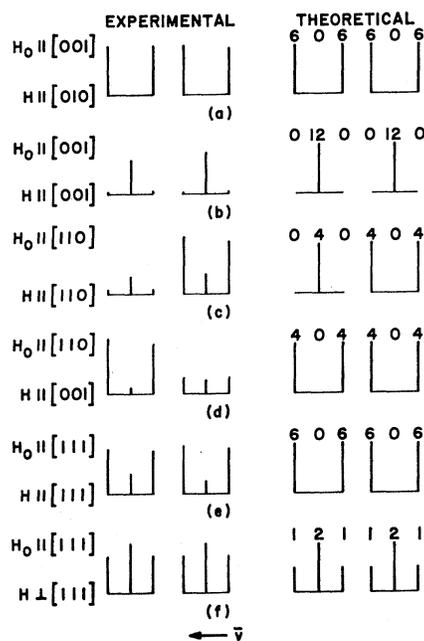


FIG. 2. Experimental and theoretical magnetic dipole intensities for the components of the transverse Zeeman patterns.

are taken from the work of Imbusch *et al.*⁹ for a magnetic dipole transition of Cr^{3+} at a tetragonal site. The theoretical intensities for $H_0 \parallel [110]$ were calculated here for a tetragonal site from the work of Sugano *et al.*⁸ This latter pattern was calculated assuming the v component of the 2E_g state lies highest in energy.

The relative intensities of the various components are in good agreement with the theoretical ones. The discrepancies between experiment and theory are most probably due to depolarization of the fluorescence by the different tetragonal domains in the crystal and by scattering of light in the experimental apparatus. A small electric dipole contribution is also possible if the site symmetry deviates from the expected C_{4h} symmetry. Relative intensities of the components for electric dipole contributions have been calculated.⁹ Comparison of the $[100]$ and $[111]$ data with the calculations shows that this mechanism cannot account for the observed discrepancies. The results for $H_0 \parallel [110]$ show that the v component lies highest in energy, indicating that the tetragonal distortion at the Cr^{3+} site is tensile.

The magnetic-field-induced splittings were linear in field up to 26 kG with a g factor of 3.94 between the outer components of the pattern for a particular line. This value implies a spin g factor for the 2E_g state which is approximately the same as that for the ground state (1.978).

In nominally pure SrTiO_3 the 8000-Å fluorescence was extremely weak but had identical linewidths and peak wavelengths at 4.2°K as the doped material, indicating that its origin is trace concentrations of Cr^{3+}

⁶ K. A. Muller, in *Paramagnetic Resonance* (Academic Press Inc., New York, 1963), p. 17.

⁷ W. Low and E. L. Offenbacher, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1965), Vol. 17.

⁸ S. Sugano, A. L. Schawlow, and F. Varsanyi, *Phys. Rev.* **120**, 2045 (1960).

⁹ G. F. Imbusch, A. L. Schawlow, A. C. May, and S. Sugano, *Phys. Rev.* **140**, A830 (1965).

ions. At higher chromium concentrations oxidation and reduction experiments¹⁰ show that the dominant optical absorption in the vicinity of 5500 Å is due to several percent of the total Cr concentration which is in the 4+ valence state.

In conclusion, the transverse Zeeman patterns of the purely electronic transition of the 8000-Å fluorescence

¹⁰ B. W. Faughnan (private communication); see B. W. Faughnan and Z. J. Kiss [Phys. Rev. Letters **21**, 1331 (1968)] for a similar effect in $SrTiO_3:Fe$.

can be consistently interpreted as the transition from the 2E_g state to the ${}^4A_{2g}$ state of the chromium ion. Below the cubic to tetragonal phase transition at 107°K the ν component of the 2E_g state lies highest in energy, indicating that the tetragonal distortion at the chromium site is tensile in nature. This result is consistent with a c/a ratio >1 in the tetragonal phase.

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Energy-Loss Straggling of a Helical Electron Beam in a Magnetized Foil

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The energy-loss process of a helical negatron or positron beam of a few MeV in a thin magnetized foil was studied. The straggling distributions were derived, taking into account spin-dependent terms of the Möller and Bhabha cross sections. These terms affect the shape of the straggling distributions by an amount which increases with increasing energy losses. Numerical calculations were carried out in some typical cases, which are of interest with a view to using the spin-polarization effect as a means of measuring the helicity of β rays.

1. INTRODUCTION

THE energy-loss straggling of a helical electron beam passing through a thin magnetized foil depends on the relative polarization of the beam and of the absorber. Recently, Braicovich¹ suggested that this effect could provide a new powerful method for β -ray helicity measurements. Since the available theoretical evaluations of the straggling² are valid in the absence of any spin-polarization effect, it has been considered worthwhile to carry out an analysis of the energy-loss process of negatrons and positrons in magnetized matter, taking into account the spin-dependent terms of the single-scattering cross section. This investigation provides the means of obtaining an evaluation of the magnitude of the polarization effect under conditions which are realistic with a view to using the effect for β -ray helicity measurements.

2. ENERGY STRAGGLING CURVE

Landau,³ in his theory of the straggling, has shown that the straggling distribution $f(\Delta, x)$, giving the probability density of an energy loss Δ suffered by a particle passing through a layer of thickness x , may be

obtained from the following expression:

$$f(\Delta, x) = \frac{1}{2\pi i} \int_{-i\infty+\sigma}^{+i\infty+\sigma} e^{p\Delta - xg(p)} dp, \quad (1)$$

where

$$g(p) = \int_0^{\epsilon_{\max}} W(\epsilon) [1 - e^{-\epsilon p}] d\epsilon. \quad (2)$$

In Eq. (2), $W(\epsilon)$ is the probability density (per unit path length) of an energy loss ϵ in a single collision, and ϵ_{\max} is the maximum energy transfer in a single collision. It is assumed that the total energy loss in the path x is small compared with the initial energy, so that the scattering process can be considered to be adequately described by the same function $W(\epsilon)$ throughout the whole succession of scatterings which cause the slowing down.

In order to apply Eq. (1) while allowing for the spin effect in the present treatment, the following approximations have been made.

(i) The "soft collisions," in which the energy transfer is of the order of the atomic binding energies, are treated in the same way as in Landau's work, and no spin effect is considered. The integration interval in Eq. (2) is accordingly split into two parts: 0, ϵ_1 and ϵ_1 , ϵ_{\max} , where ϵ_1 is the separation energy defined by Landau. The integral in the first interval is calculated by replacing the exponential $e^{-p\epsilon}$ with $1 - p\epsilon$. As a con-

¹ L. Braicovich, Letters Nuovo Cimento **1**, 340 (1969).

² See R. D. Birkhoff, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 34, p. 53.

³ L. D. Landau, J. Phys. USSR **8**, 201 (1944).