Magneto-Optical Effects in the Paramagnetic and Ferromagnetic Phases of $CrBr_3$

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We report new measurements of thermoreflectance spectra of $CrBr_3$ in the paramagnetic and ferromagnetic phases in the 2.5–4 eV region. The spectra obtained with use of unpolarized and circularly polarized light, with and without external magnetic field, allow one to identify the dominating modulation mechanisms: electron-phonon interaction modulation (shift and broadening effects) in the paramagnetic phase, and exchange interaction modulation (splitting effects) in the ferromagnetic phase.

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In this Letter we present new results on the optical properties of the ferromagnetic insulator $CrBr_3$ below T_c ($T_c = 32.5$ K [1]) obtained from thermoreflectance (TR) measurements using circularly polarized light and with an external saturating magnetic field. This technique, named magnetothermoreflectance (MTR), allows one to resolve complex structures into their polarized components and also to study the modulation mechanisms of the optical spectra operative above and below T_c.

The intra-atomic (*d-d* or *f-f* transition) optical spectra of magnetic insulators, which display a critical change at the magnetic phase transitions, have been intensively investigated during the last fifteen years. Few data exist concerning the magnetic effects on the optical properties in the spectral region beyond the intra-atomic one, which seems to involve both localized and band states (charge transfer, orbital promotion, and band-to-band transitions). Only recently a variety of modulation techniques for observing such optical spectra have been reported.[2-7] With regard to thermoreflectance, recent results have shown that near T_c TR spectra exhibit remarkable changes due not only to the normal electron-phonon interaction but also to the beginning of the magnetic ordering (for instance, effects due to the exchange interaction, oscillator strength transfer, and symmetry reduction in the magnetic lattice).

Different modulation mechanisms have been proposed in order to interpret the fine structures and their line shapes observed in the TR spectra. However, a general discussion of the spectra in the magnetic phase is lacking.

The previously reported TR measurements were generally done without orienting external magnetic field and with use of unpolarized light, whereas MTR measurements are to be preferred because they provide unambigous data and additional tests of the theoretical interpretation.

TR spectra of $CrBr_3$ in the vacuum-ultraviolet region[6,7] are an example where it is difficult to identify the modulation mechanisms. In fact it has been observed that some structures show an abrupt change of line shape and intensity near T_c. In order to explain these features it has been proposed[8] that the exchange-splitting modulation effects become predominant over the electron-phonon interaction, passing from the paramagnetic to the ferromagnetic phase.

Here we present a proof of the validity of the line splitting model in the case of $CrBr_3$ crystals by studying the MTR spectra in the region around 3.5 eV, where the reflectance spectrum presents two predominant bands at 3.10 and 3.75 eV (at liquid-nitrogen temperature).[6] We have performed the measurements in the Faraday geometry with an external saturating magnetic field ($H = 6$ kOe) parallel to the c axis of the crystal. The physical and chemical properties of $CrBr_3$ are extensively reported in Ref. 1; the main features of the TR apparatus have been discussed elsewhere.[6] A temperature modulation ΔT of no more than 0.5 K has been used and the approximate size of $\Delta R/R$ in the peaks was 5×10^{-3}. Monochromatic light was circularly polarized by a Rochon prism and a quartz Babinet-Soleil compensator ($|E_y/E_x|^2 \geqslant 0.9$, where $\vec{E}$ is the electric wave vector).

In Fig. 1 the TR spectra at $T > T_c$ ($T = 80$ K, $\Delta T \simeq 0.5$ K) for right- and left-circularly polarized

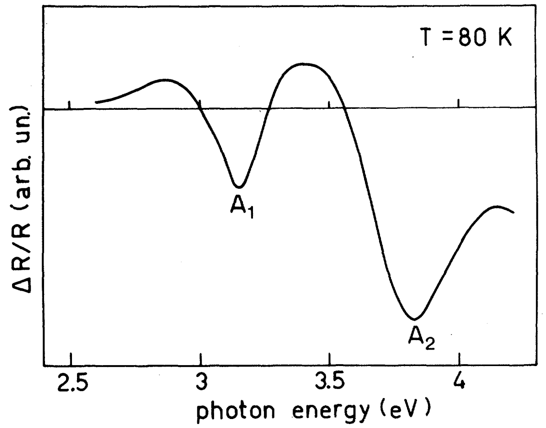

FIG. 1. TR spectrum of $CrBr_3$ in the paramagnetic phase.

light are presented. Obviously, the two spectra coincide in the paramagnetic phase and reproduce the unpolarized spectrum. They can be interpreted as due to the modulation of the electron-phonon interaction. In Figs. 2(a) and 2(b) the TR spectra at $T<T_c$ ($T=25$ K, $\Delta T \simeq 0.1$ K) for right- and left-circularly polarized light are presented, respectively, with the same vertical scale as in Fig. 1. Let us focus our attention on the first structures only; it is evident that the band A_1 is split by the molecular field into A_{1-} and A_{1+} bands. From the respective zero-crossing points we obtain the energy of the split bands: $A_{1-}=2.88$ eV and $A_{1+}=2.98$ eV, both with a bandwidth $\Gamma \simeq 0.3$ eV. The splitting energy would be $\simeq 0.1$ eV, which is much larger than the value obtained from absorption-edge measurements with polarized light.[9]

The A_1 peak is interpreted as an allowed electronic transition from the ${}^4A_{2g}$ ground state to an excited state with ${}^4T_{2u}$ symmetry (in particular, an electron transfer transition in which an electron from an halogen ion is removed to the Cr^{3+} ion).[9] At temperatures far below T_c, the exchange field will remove the spin degeneracy of the ${}^4A_{2g}$ ground state with the result that only the state $m_s=-\frac{3}{2}$ is occupied. Allowed electric dipole transitions will be possible to excited states ($m_l=\pm 1$, $m_s=-\frac{3}{2}$) with ${}^4T_{2u}$ symmetry. In Ref. 9 it was proposed that the splitting to the A_{1+} and A_{1-} structures arises from the spin polarization of the initial state and from the spin-orbit interaction of the final state only, neglecting the exchange-field effect on the excited states. Thus the difference between the absorption band edges, corresponding to the two different circular polarizations for this optical transition, was calculated to be of the order of 100 cm^{-1} (0.012 eV). The experimental value obtained was of the order of 200 cm^{-1} (0.025 eV), at 1.5 K. Our experimental energy difference of the two MTR optical features, derived from the zero-crossing points of the spectra, is better correlated to the overall optical structure (but it neglects broadening effects). Moreover our measurements are performed at 25 K. For a better understanding and comparison of the two data, we are planning to repeat the measurement at liquid-helium temperature and extract the energy of the transitions by a best fit of our MTR spectra, taking into account some broadening effect also. At this time, because of experimental problems, this is impossible for us.

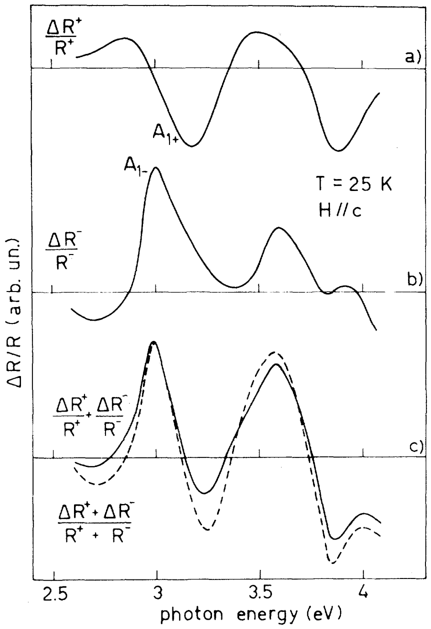

FIG. 2. TR spectra of $CrBr_3$ in the ferromagnetic phase, in the Faraday geometry with an external magnetic field of 6 KOe, $\vec{H} \| \vec{c}$. (a), (b) Right- and left-circularly polarized light, respectively; (c) sum of the two spectra in (a) and (b) (solid line) and TR spectrum for unpolarized light and $H=0$ (broken line).

However, an important consideration can be made at this point as regards the physical model of Ref. 9, in which the spin-orbit interaction in the ${}^4T_{2u}$ state plays an essential role in producing the splitting of the energy levels: We remark that this model should work at temperatures low enough so that only the lowest ground-state sublevel is significantly populated. Our experimental results give evidence that, just below T_c, large magneto-optical effects are present. This suggests that the exchange splitting of the excited state is to be considered as well as the spin-orbit interaction (and the thermal population of the ground-state sublevels also).

For a better understanding of the dominating modulation mechanisms either for $T > T_c$ or for $T < T_c$, in Fig. 3 we report the theoretical line shapes obtained by singly modulating the parameters which characterize the reflectivity structure associated with a damped Lorentz oscillator. Thus the complex dielectric constant $\tilde{\epsilon}$ for $T > T_c$ is given by

$$\tilde{\epsilon} = \epsilon_\infty + \frac{1}{\nu_0^2 - \nu^2 + i\Gamma\nu},$$

and for $T < T_c$, and for circularly polarized light, by

$$\tilde{\epsilon}_\pm = \epsilon_\infty + \frac{1}{\nu_0^2 - \nu^2 \pm 2\nu\nu_L + i\Gamma\nu},$$

where the splitting $2\nu_L$ describes the effect of the exchange interaction.[10]

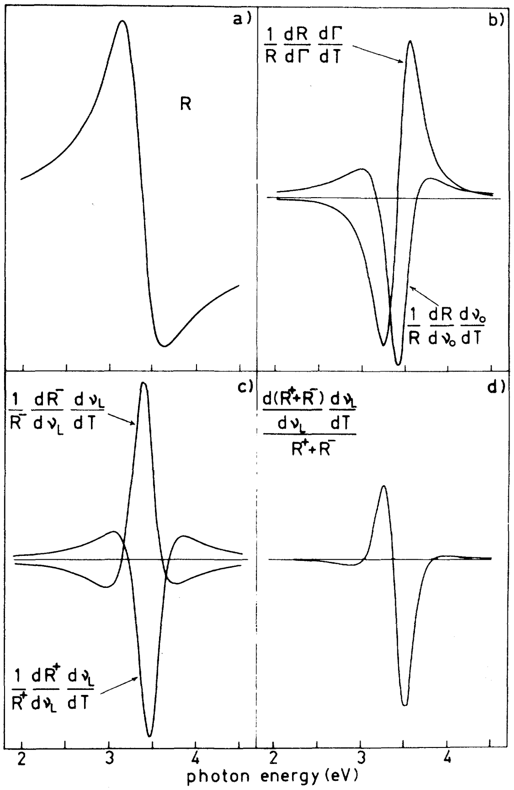

FIG. 3. Reflectance (R) and thermoreflectance $[R^{-1}(dR/dx)dx/dT$, where $x = \nu_0, \Gamma, \nu_L]$ line shapes associated with a damped Lorentz oscillator. The simbols + and − refer to the right- and left-circularly polarized light, respectively. The vertical scale is in arbitrary units. In all the curves the parameter values, which fit well the A_1 structure in $CrBr_3$ reflectance, are $\epsilon_\infty = 4.65$, $h\nu_0 = 3.2$ eV, $\hbar\Gamma = 0.4$ eV, $h\nu_L = 0.05$ eV, and oscillator strength $f = 7.3$ eV^2. In addition, it is assumed that $d\Gamma/dT > 0$, $d\nu_0/dT < 0$, $d\nu_L/dT < 0$.

From a comparison between Fig. 1 and Fig. 3(b) it follows that for $T > T_c$ the main mechanism is a modulation of the peak energy ν_0 (with $d\nu_0/dT \simeq -1.5\times 10^{-3}$ eV/K[6]) associated with the electron-phonon interaction. For $T < T_c$, from Figs. 2(a) and 2(b) and Fig. 3(c) it follows that the spin order modulation effect $(d\nu_L/dT)$ is predominant. The main spectral features are to be understood in terms of coupled Lorentzian line shapes correlated with electronic transitions split by the molecular field and electric dipole allowed for right- and left-circularly polarized light. The coupled structures present modulation temperature coefficients of opposite signs which converge to zero as $T \to T_c$.

In Fig. 2(c) we compare the sum of the two spectra of Figs. 2(a) and 2(b) $(T < T_c)$ obtained for differently circularly polarized light with that obtained experimentally with unpolarized light and without external magnetic field. The agreement between the two curves is excellent as one should expect since

$$R_{\text{unp}} \simeq R_+ \simeq R_-,$$

and then

$$\left(\frac{\Delta R}{R}\right)_{\text{unp}} = \frac{\Delta R_+ + \Delta R_-}{R_+ + R_-} \simeq \frac{1}{2}\left(\frac{\Delta R_+}{R_+} + \frac{\Delta R_-}{R_-}\right).$$

From Fig. 2(c) and Fig. 3(d) one can see that, with use of unpolarized light, the change of the TR line shape for $T > T_c$ and for $T < T_c$ is well explained by a superposition of two very close structures, with temperature coefficients of opposite sign. The modulation model proposed to explain the TR spectra features of EuO,[2,3] does not work in our case. In fact in that model the spectral shapes, intensity, and relative energy shifts of the exciton-related fine structures are discussed in terms of the spin polarization and spin-disorder scattering effects of the nonlocal Bloch electrons. In the TR spectra the dominant modulation mechanism is supposed to arise from the anomalous thermal changes in the energy and in the damping constant of the electronic transitions at T_c and should give equal spectra for different circular polarizations (under the assumption that the transition takes place for both polarizations).

From reported experimental results it appears that the MTR measurements with circularly polarized light supply unambiguous and clearer information compared with TR with unpolarized light, both on the polarization state of the optical lines and on the exchange splitting of the electronic transitions. Measurements are in progress for extending the spectral range to the ultraviolet region and for studying the behavior of the MTR spectrum versus the temperature. Moreover, by a suitable best fit of the optical features of the spectrum it will be easier to follow the temperature dependence of the energy position and line shape in order to gain information about the dynamical spin fluctuation effect on the electronic state.

Also in order to determine in the case of the Eu chalcogenides the modulation mechanisms which affect the optical structures near T_c and their relative weights, MTR measurements at different temperatures are in progress on EuO.

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"Spin-Doping," a New Tool in Electronic Band Structure Investigation

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"Spin doping" by paramagnetic ions adds to the electronic g factor of charge carriers in semiconductors, a temperature sensitive part, so that by means of the artificial temperature dependence any intraband resonance transition can be identified unambiguously.

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Optical resonance spectroscopy is a powerful means for the investigation of the electronic energy-band structure of solids. Submillimeter magnetospectroscopy especially provides detailed information on the intraband energy separation of the Landau levels in the presence of an external magnetic field, assuming that the initial and final states of the resonance transition are unambiguously identified. This identification, however, is often somewhat arbitrary. For a more complicated band structure it is generally not possible to distinguish between a combined spin flip (CSF) and a pure spin flip (SF) by means of polarization-dependent selection rules, as shown schematically in Fig. 1. Also, the study of the temperature dependence of the resonance

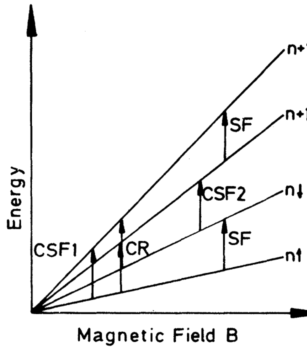

FIG. 1. The scheme for different magnetoresonances shows that pure spin-flip and combined spin-flip transitions may have about the same resonance position and then are difficult to distinguish.