Optical Evidence for a Spin-Filter Effect in the Charge Transport of Eu$_{0.6}$Ca$_{0.4}$B$_6$

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(Received 7 May 2003; published 10 February 2004)

We have measured the optical reflectivity $R(\omega)$ of Eu$_{0.6}$Ca$_{0.4}$B$_6$ as a function of temperature ($T$) between 1.5 and 300 K and in external magnetic fields ($H$) up to 7 T. $R(\omega)$ increases with decreasing $T$ and increasing $H$ field, but the plasma edge feature does not exhibit the sharp onset and steep slope that is observed in EuB$_6$. The analysis of the $H$-field dependence of the low-$T$ optical conductivity confirms the previously observed exponential decrease of the electrical resistivity upon increasing bulk magnetization at constant $T$. The individual exponential magnetization dependences of the plasma frequency and scattering rate are also extracted from the optical data.

DOI: 10.1103/PhysRevLett.92.067401 PACS numbers: 78.20.Ls, 75.50.Cc

Remarkable variations of electronic transport properties, distinctly depending on the bulk magnetization, have been observed for materials, such as rare-earth hexaborides and manganites [1,2]. A very direct link between electronic transport and bulk magnetization $M$ [3,4] was revealed by measurements of magneto-optical properties [5,6] of ferromagnetic EuB$_6$, exhibiting a substantial blue shift of the plasma edge in the optical reflectivity with decreasing temperature and increasing magnetic field $H$.

More recently, dc magnetotransport and magnetization experiments on a series of Eu$_{1-x}$Ca$_x$B$_6$ compounds provided results that again reflect the intimate relation between the electronic conductivity and the magnetization. In particular, for the material with $x = 0.4$, an exponential decrease of the resistivity $\rho_{dc}$ as a function of magnetization at constant temperature close to and below the Curie temperature $T_C = 4.5$ K was reported [7]. These observations are unusual for a bulk magnetic material. Based on these results it was suggested that some kind of magnetization-dependent barriers or intrinsic spin-filter effects dominate the electronic transport in the magnetically ordered phase of this material [7]. Spin-filter effects have recently stimulated both experimental and theoretical activities and, in particular, are discussed in connection with stacked thin film systems exhibiting giant magnetoresistance [8] and with specially tailored hybrid layer systems providing filter tunnel barriers [9].

In this respect, Ca-doped EuB$_6$ seems to be a promising prototype bulk material, and it is therefore of interest to further characterize its charge transport by investigating the electrodynamic response. Since $\rho_{dc} \sim \Gamma/\omega_p^2$, where $\Gamma$ and $\omega_p$ are the scattering rate and the plasma frequency of the itinerant charge carriers, respectively, it is instructive to single out the relevance of those quantities in relation with the dc properties. The measured optical response and its phenomenological analysis, based on the classical dispersion theory, offer this possibility and provide information on important electronic parameters, including the disorder-induced scattering rate of the charge carriers.

The single crystal of Eu$_{0.6}$Ca$_{0.4}$B$_6$ was prepared by solution growth from Al flux, using the necessary high purity elements as starting materials. Our specimen (1.7 $\times$ 1.7 $\times$ 0.5 mm$^3$) is from the same batch of samples described in Ref. [7]. From the absence of any sharp features in $\rho_{dc}(T)$ at 1.2 K, the critical temperature for the superconductivity of Al, we exclude the presence of Al inclusions in the sample [7]. The optical reflectivity $R(\omega)$ was measured in a broad spectral range from the far infrared (FIR) to the ultraviolet and as a function of both temperature and magnetic field. The corresponding experimental details are described in Refs. [5,6].

Figure 1 summarizes the relevant $R(\omega)$ results, at selected temperatures from above to below $T_C$ and as a function of the external magnetic field. We limit our presentation to the spectral range from FIR up to the midinfrared, where the field and temperature induced variations of $R(\omega)$ are most prominent. Around 5000 cm$^{-1}$ all recorded $R(\omega)$ spectra merge and above 50 K no field dependence is observed. A comparison with previously published data for EuB$_6$ [6] reveals distinct differences. Although $R(\omega)$ is still of the metallic type, the onset of its plasma edge in zero field is broad in Ca-doped EuB$_6$, i.e., a much less sharp feature than the increase of $R(\omega)$ with decreasing $\omega$ for EuB$_6$. The apparent blueshift of $R(\omega)$ with increasing field in the present case is rather the result of an increasing slope of $R(\omega)$ at the onset of the upturn than a total shift of the edge as observed in EuB$_6$ [6]. These differences are exemplified by the reproduction of the zero field $R(\omega)$ at 50 and 1.6 K for $x = 0$ [5,6] in Fig. 1(a). The peak at about 150 cm$^{-1}$ is an optically active phonon [5]. A closer inspection of the data reveals a small shift of this phonon mode to lower frequencies at temperatures below 6 K. The other infrared active phonon, observed around 850 cm$^{-1}$ in EuB$_6$ [5,6], can barely be identified here. It appears as a tiny spike.
Unexpected and puzzling is the temperature dependence of $R(\omega)$ in zero field, shown in Fig. 1(a). At the lowest experimentally accessible frequency, $R(\omega)$ is consistent with the HR extrapolation using, however, $\sigma_{dc}$ values in zero field that are not in agreement with those of Ref. [7]. The $\sigma_{dc}$ values used in the HR extrapolation increase instead of decreasing by a factor of 4 between 20 and 2 K. Inserting the $\sigma_{dc}$ values of Ref. [7] would imply that $R(\omega)$ at low frequencies and in zero field decreases with decreasing temperature. This is not compatible with the experimental findings, at least above 30 cm$^{-1}$ [Fig. 1(a)]. Optical experiments in the microwave range, i.e., below 30 cm$^{-1}$, may eventually solve this puzzle and reconcile the optical results with the dc transport properties. Our interest here, however, is focused on the relative magnetic field dependence, which does not suffer from any inconsistencies between dc and dynamical properties. Therefore, we have not attempted to extrapolate the optical data in zero field by forcing an agreement with the corresponding $\sigma_{dc}$ of Ref. [7]. As will be clear below, our choice for $\sigma_{dc}$ in zero field neither alters the main content of our discussion nor does it affect the conclusion of our work.

The Kramers-Kronig transformations [10] of $R(\omega)$ allow us to extract the optical functions, such as the real part $\sigma_1(\omega)$ of the optical conductivity. As an example we show $\sigma_1(\omega)$ at 10 K and 7 T in Fig. 2. At low frequencies one can easily recognize the metallic component of $\sigma_1(\omega)$, where the limit $\sigma_1(\omega \rightarrow 0)$ reflects the dc conductivity [12]. Above 300 cm$^{-1}$ and up to the midinfrared, $\sigma_1(\omega)$ saturates to an almost constant value. Above $10^4$ cm$^{-1}$ (inset of Fig. 2) we note the clear onset of interband transitions [5,6]. The $R(\omega)$ and $\sigma_1(\omega)$ spectra, for any combination of temperature and magnetic field, can be well reproduced by employing the Lorentz-Drude model based on the classical dispersion theory [6,10]. Figure 2 reveals the individual components considered for the fit. At all temperatures and fields the same number of fit components were considered. Apart from two temperature and field independent Lorentz harmonic oscillators (h.o. 2 and 3) in the frequency range above $1.6 \times 10^4$ cm$^{-1}$ (2 eV), we introduced a temperature and field-dependent h.o. 1 at about 9900 cm$^{-1}$ (1.2 eV). The latter Lorentz h.o. may phenomenologically be interpreted as to reflect the 4f-5d electronic interband transitions [5,13]. Also the phonon mode at 150 cm$^{-1}$ was described with a h.o. In order to account for the optical properties in the far and midinfrared spectral range (i.e., $\omega < 3000$ cm$^{-1}$), two-Drude resonances must be considered. For simplicity, we call them the first Drude (D1) and the second Drude (D2) term, respectively. The total spectral weight encountered in the metallic component of $\sigma_1(\omega)$, i.e., the sum of the squared plasma frequencies of the two-Drude terms, defines the effective plasma frequency of Eu$_{0.6}$Ca$_{0.4}$B$_6$. The two-Drude terms suggest a scenario where two different types of charge carriers exist. Those charge carriers belong to two bands (e.g., a
The three harmonic oscillators (h.o.) are differently affected by the ferromagnetic transition, i.e., are differently coupled to the spin system (see below), and are characterized by distinct scattering rates and effective masses.

We fit the frequency dependence of both $R(\omega)$ and $\sigma_1(\omega)$ by allowing for changes of the plasma frequency of both Drude terms ($\omega_p^{D1}$ and $\omega_p^{D2}$, respectively), of the strength of the h.o. 1 ($\omega_{p1}$), and of the scattering rate ($\Gamma_1$) of the first Drude term [11]. The first Drude term is characterized by a rather small, temperature and field-dependent scattering rate ($\Gamma_1$). The second Drude component mainly accounts for the spectral weight background of $\sigma_1(\omega)$ causing the shoulder most prominently seen at 1000 cm$^{-1}$ in $R(\omega)$ at low temperatures and high fields (Fig. 1). Its scattering rate ($\Gamma_2$) is large and does not vary with temperature and field. Upon decreasing temperature or increasing field, both Drude terms gain spectral weight, which is shifted down from higher energies, i.e., from the h.o. 1. The total spectral weight is however conserved, satisfying the optical sum rule. As a consequence of the increasing screening by the itinerant carriers, the phonon mode component disappears with increasing field or decreasing temperature.

Figure 3 captures the main results of this study. In Fig. 3(a) we plot $1/(\omega_p^{D1})^2$ as a function of $M$ [14], while Fig. 3(b) shows the scattering rate $\Gamma_1(M)$ of the first Drude term [15]. At all temperatures below 30 K, we find that these two quantities may be well described by

$$\left[\omega_p^{D1}(M)\right]^{-2} = (\omega_{p0})^{-2} e^{-\beta_\omega M} \quad (1)$$

and

$$\Gamma_1(M) = \Gamma_0 e^{-\beta_1 M}, \quad (2)$$

where $\omega_{p0}$ and $\Gamma_0$ as well as $\beta_\omega$ or $\beta_1$ are constants whose values are listed in the caption of Fig. 3. The functional form of Eq. (1) is the best possible choice to fit the Drude weight variation. The choice of $[\omega_p^{D1}(M)]^2$ varying linearly with $M$ (as for EuB$_6$ [6]) is obviously inadequate. From the Lorentz-Drude fit parameters we can calculate the conductivity at $\omega = 0$ from $\sigma_1(\omega = 0) = \sigma_1^{D1}(\omega = 0) + \sigma_1^{D2}(\omega = 0) = \sigma_{dc}$, and $\rho_{dc} = 1/\sigma_{dc}$.
Figure 3(c) shows the $\rho_{dc}$ values, normalized by $\rho_{dc}(M = 0)$ at each temperature, as a function of $M$. On purpose we have chosen the same representation of $\rho_{dc}(M)/\rho_{dc}(M = 0)$ versus $M$ as first suggested empirically in Ref. [7].

It may immediately be seen from Fig. 3(c) that the expression

$$\rho_{dc}(M) = \rho_{dc}(M = 0)e^{-\beta M} \quad (3)$$

describes very nicely the $\rho_{dc}$ values calculated from the Lorentz-Drude fit parameters at $\omega = 0$. It turns out that the best fit to the data points in Fig. 3(c) employing Eq. (3) is very close to the product of Eqs. (1) and (2), such that $\beta = \beta_0 + \beta_1$. Both $\beta_1$ and $\beta_0$ are of equal magnitude, suggesting that Eqs. (1) and (2) are of equal importance in shaping the exponential behavior of Eq. (3). The difference in $\rho_{dc}(M)/\rho_{dc}(M = 0)$ for temperatures below 6 K and well above $T_C$ is mainly due to the differences of the corresponding scattering rates ($\Gamma_1$) [Fig. 3(b)]. Therefore, the first Drude term is the most relevant component in determining the dc ($\omega \rightarrow 0$) transport properties and governs to a great extent the temperature and magnetic field dependence of $\sigma_t(\omega)$ at low frequencies. Although the total spectral weight of both Drude terms has been considered in Fig. 3(c), the contribution of the second Drude term is only of marginal relevance with respect to the dc properties.

The two temperature regimes identified in Fig. 3(c) for temperatures below 6 K and well above $T_C$ have been found in Ref. [7] as well, even though $\rho_{dc}(M)/\rho_{dc}(M = 0)$ was larger at 12 K than at 2 K (see Fig. 4 in Ref. [7]). This is the consequence of using the $\rho_{dc}(M = 0)$ values for the normalized representation in Fig. 3(c) as they follow from the optical results. These values at zero field, as stated above, do not track the measured dc transport data [7].

Wigger et al. suggested that some intrinsic $M$-dependent spin-filter effect dictates the electronic conduction in this material. The exponential variation of $\rho_{dc}(M)$ [Eq. (3)] was viewed as being due to magnetization-dependent tunnel barriers, caused by the domain walls of the ferromagnetically ordered phase in zero external field, which limit the motion of electrons. The domain walls are thought to be favored by the disorder on the cation sublattice and to be progressively weakened and removed upon increasing $M$ [7]. This disorder is most likely also responsible for the rather broad onset of the plasma edge feature in $R(\omega)$, at least at high temperatures and low fields (Fig. 1). The results and the conclusions which follow from the analysis of the optical data (Fig. 3) confirm the results obtained in the previous investigation of dc magnetotransport properties [7]. In addition, however, they allow for an analysis of the individual $M$ dependences of the two quantities that determine the dc transport, i.e., the plasma frequency and the scattering rate. The exponential variations that link $M$ to the Drude spectral weight, which is proportional to the ratio $n/m$ of the charge carrier concentration ($n$) and the effective mass ($m$), and to the scattering rate, are rather intriguing. It remains to be seen how these findings can be explained on a microscopic level.

The authors thank J. Müller for technical help and G.A. Wigger and R. Monnier for fruitful discussions. This work has been supported by the Swiss National Foundation for the Scientific Research.

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[12] Although not shown explicitly, we note that the low frequency part ($\omega < 300$ cm$^{-1}$) of $\sigma_t(\omega)$ narrows with decreasing temperature and increasing field. This is the consequence of the enhanced $R(\omega)$ at low frequencies with increasing field and decreasing temperature (Fig. 1).
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[14] $M$ has been measured up to 5.5 T (Ref. [7]). By assuming a Brillouin function for the overall behavior of $M(H, T)$, a simple fit of the measured $M$ data leads to the values of $M$ at 6 and 7 T for different temperatures. These values were combined with the corresponding optical parameters ($\omega_p$ and $\Gamma$), obtained from the optical spectra up to 7 T.
[15] At the highest field and lowest temperature the width of the effective metallic component in $\sigma_t(\omega)$ is of the same order of magnitude as our experimental low frequency limit and the resulting scattering rate of the first Drude term might be slightly overestimated. The excellent fit quality of $R(\omega)$ based on the Lorentz-Drude model across the entire measured spectral range [Fig. 1(d)] and the overall good agreement of $\Gamma_1$ with the exponential behavior [Eq. (2)], for all combinations of fields and temperatures, strongly support the validity of our fit procedure.