

**Electronic transport in EuB<sub>6</sub>**

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EuB<sub>6</sub> is a magnetic semiconductor in which defects introduce charge carriers into the conduction band with the Fermi energy varying with temperature and magnetic field and which orders ferromagnetically via two consecutive phase transitions at 15.5 and 12.5 K, respectively. We present a consistent analysis of the temperature- and magnetic-field dependences of the electrical resistivity and of the Hall effect of a single-crystalline sample at temperatures between 22.5 and 300 K, as well as between 2 and 8 K, avoiding the critical transition region. The covered magnetic-field range was between 0 and 5.5 T. The negative magnetoresistance is well reproduced by a model in which the spin disorder scattering is reduced by the applied magnetic field. The Hall effect can be separated into an ordinary and an anomalous part. At 22.5 K the latter accounts for half of the observed Hall voltage, and its importance decreases rapidly with increasing temperature. As for Gd and its compounds, where the rare-earth ion adopts the same Hund's rule ground state as Eu<sup>2+</sup> in EuB<sub>6</sub>, the standard antisymmetric scattering mechanisms underestimate the *size* of this contribution by several orders of magnitude, while reproducing its *shape* almost perfectly. Well below the bulk ferromagnetic ordering at  $T_C = 12.5$  K, a two-band model successfully describes the magnetotransport. Our description is consistent with published de Haas–van Alphen, optical reflectivity, angular-resolved photoemission, and soft x-ray emission as well as absorption data, but requires a new interpretation for the gap feature deduced from the latter two experiments.

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**I. INTRODUCTION**

The binary compound EuB<sub>6</sub> crystallizes in a simple cubic lattice, with divalent Eu ions in their <sup>8</sup>S<sub>7/2</sub> Hund's rule ground state at the corners of the unit cell and B<sub>6</sub>-octahedra centered at the body-centered positions. With decreasing temperature, it orders ferromagnetically<sup>1</sup> via two consecutive phase transitions at ~15.5 K and ~12.5 K, respectively,<sup>2</sup> the first of which has recently been interpreted as a phase separation between small magnetically ordered regions with mobile charge carriers and large disordered regions with localized magnetic polarons.<sup>3</sup> A spin-polarized electronic-structure calculation in the local spin-density approximation for exchange and correlation (LSDA) correctly reproduces the lattice constant, the internal coordinates of the boron atoms, and the size of the magnetic moment in the stoichiometric compound.<sup>4</sup> It also predicts the system to be a semi-metal, with overlapping conduction and valence bands around the X-point of the Brillouin zone (BZ), in contradiction with the results of a combined study based on angle-resolved photoemission (ARPES) and bulk-sensitive soft x-ray emission (SXE) and absorption (XAS) spectroscopies,<sup>5</sup> which suggest a gap of at least 1 eV between the two bands. While, given the approximation used in the calculation, this discrepancy is not surprising, the fact that conduction-band states were observed at all in the photoemission experiment, illustrates the fundamental problem one is faced with when trying to describe the transport properties of this system and of the hexaborides in general, namely, that their behavior is to a large extent determined by defects and impurities.<sup>6,7</sup>

In this paper, we offer a quantitative analysis of magneti-

zation, magnetoresistance, and Hall effect data, obtained on one and the same sample, using a plausible model for the origin of the mobile charge carriers and a consistent description of the dependence of their concentration and their scattering rate on the applied magnetic field and on temperature. Explicitly, we consider EuB<sub>6</sub> to be a strongly compensated *n*-type magnetic semiconductor. Due to the merging of defect states, i.e., boron vacancy levels, with the conduction band, the latter acquires a certain concentration of charge carriers, as evidenced by ARPES.<sup>5</sup> In the paramagnetic state and in the absence of external magnetic fields, these are equally distributed over six pockets (three for each spin direction) centered at the X points of the BZ. Due to the thermal ionization of deep trap states in the gap, the occupation of these states increases slightly with temperature. The exchange coupling between the conduction electrons and the localized (spin-) magnetic moments of the Eu ions leads to a lowering of the conduction-band edge above  $T_c$  and to a splitting of the spin-up and spin-down bands below  $T_c$ .<sup>4,8,9</sup> It is also responsible for the so-called spin-disorder resistivity<sup>9–13</sup> which, in a semiconductor, is strongly dependent on the degree of spin polarization of the conduction electrons and on the concomitant redistribution of the charge carriers between the spin-up and spin-down bands.<sup>9</sup> We have attempted to model our data on the anomalous Hall effect with the mechanism suggested by Kondo<sup>13</sup> for the case of gadolinium metal, where the trivalent Gd ions adopt the same  $4f^7$  configuration as Eu<sup>2+</sup> in EuB<sub>6</sub>. We have generalized this approach to include inelastic spin-flip processes. As in this previous work, we find that the shape of the calculated field and temperature dependences of the anomalous Hall resistivity curves

matches that of the measured ones almost perfectly, but the magnitude of the effect resulting from the calculation is several orders of magnitude too small, if reasonable values for the parameters are used in the theory. An alternative mechanism proposed by Maranzana,<sup>14</sup> namely, the interaction between the orbital motion of the conduction electrons and the localized moments, leads to the same functional dependence of  $\rho_H$  on temperature and applied field, but with an even smaller amplitude.

## II. SAMPLE AND EXPERIMENTAL SETUP

The single-crystalline sample of  $\text{EuB}_6$  was prepared by solution growth from Al flux. All measurements were made using the same platelet type specimen with dimensions of approximately  $4.8 \times 5.2 \times 0.25 \text{ mm}^3$ . The room-temperature lattice constant of  $4.185 \text{ \AA}$  was evaluated from x-ray powder-diffraction data, using a least-square refinement based on Cohen's method, with the software Xlat.<sup>15</sup> A Si spectrum served as the internal standard. Gold wires with  $25 \text{ }\mu\text{m}$  diameter were contacted to the sample with silver epoxy. All voltages were measured with a four-probe, low-frequency ac technique in the Ohmic regime. The transverse magnetoresistance, which in the following is always referred to as the magnetoresistance, and the Hall voltage  $V_H$  were measured in a configuration where the external field  $\vec{B}_a$ , between 0 and 5.5 T, was oriented perpendicularly to both the applied current and the measured voltages, thus orthogonal to the platelet. The extended temperature range was covered by using a conventional  $^4\text{He}$  cryostat. Magnetization measurements were made in the same geometry with a commercial superconducting quantum interference device (SQUID) magnetometer, reaching temperatures between 2 and 330 K and magnetic fields up to 5.5 T.

## III. ELECTRICAL TRANSPORT ABOVE 20 K

### A. Theory

The unperturbed conduction-electron levels are approximated by parabolic bands, centered at the  $X$ -points of the BZ, with spin independent and, for convenience, isotropic effective masses  $m^*$ . The energies of the band bottoms are specified by  $\epsilon_0^s$ , where  $s = \pm$  labels the spin of the electron. The corresponding Bloch states are denoted as  $|i\vec{k}s\rangle$ , where  $i = 1, 2, 3$  specifies the  $X$ -point from which  $\vec{k}$  is measured.

Following Haas,<sup>9</sup> we denote the eigenstates of the system of magnetic Eu ions by  $|\alpha\rangle$  and their occupation probabilities by  $w_\alpha$ , so that, for example, the equilibrium value of the  $z$  component of the spin of the ion located at the site  $\vec{R}_n$  is given by

$$\langle S_{nz} \rangle = \sum_{\alpha} w_{\alpha} \langle \alpha | S_{nz} | \alpha \rangle. \quad (1)$$

Our magnetization measurements show that above  $\sim 20 \text{ K}$  and up to fields of 6 T, this quantity is well described by molecular field theory and in the following, we shall as-

sume that in this temperature range, this also applies to higher-order correlation functions.

The exchange interaction between the magnetic moments and the mobile charge carriers has the form

$$\mathcal{H}_1 = - \sum_{n=1}^N J(\vec{r} - \vec{R}_n) \vec{s} \cdot \vec{S}_n, \quad (2)$$

where the sum is over all unit cells in the crystal, and  $\vec{s}$  is the spin of the conduction electron at  $\vec{r}$ . The range of  $J(\vec{r})$  is determined by the radius of the  $4f$  shell.

To first order in perturbation theory, this interaction produces the following modification in the energy eigenvalues of the band electrons

$$\begin{aligned} \Delta \epsilon_s^{(1)}(\vec{k}) &= \sum_{\alpha} w_{\alpha} \langle i\vec{k}s; \alpha | \mathcal{H}_1 | i\vec{k}s; \alpha \rangle \\ &= - \sum_{n=1}^N \langle i\vec{k} | J(\vec{r} - \vec{R}_n) | i\vec{k} \rangle \cdot \langle s | \vec{s} | s \rangle \\ &\quad \times \sum_{\alpha} w_{\alpha} \langle \alpha | \vec{S}_n | \alpha \rangle. \end{aligned} \quad (3)$$

For a collinear ferromagnet, such as  $\text{EuB}_6$ , the average value embodied in the last sum points along the magnetization axis, which we choose as the quantization axis for the conduction-electron spins. Furthermore, all magnetic ions being equivalent, we can define

$$J_{i\vec{k}} = N \langle i\vec{k} | J(\vec{r}) | i\vec{k} \rangle \approx J, \quad (4)$$

where, in the last step, we have used the effective mass approximation.

The spin-dependent energy shift then takes the form

$$\Delta \epsilon_s^{(1)} = - \frac{1}{2} s J \sigma, \quad (5)$$

where the mean ionic spin  $\sigma = S(M/M_{\text{sat}})$  depends on temperature and magnetic field.  $M_{\text{sat}} = -(N/V)g\mu_B S$  is the saturation magnetization per unit volume,  $V$  is the volume of the sample,  $\mu_B$  is the Bohr magneton, and  $g$  is the  $g$  factor of the magnetic ion with spin  $S$ .

The second-order correction is independent of the spin of the conduction electrons in the absence of a net magnetization and is completely dominated by the first-order splitting [see Eq. (5)] otherwise, so that it may safely be neglected in the discussion of magnetotransport properties.

The generic form for the matrix element of the interaction  $\mathcal{H}_2$  responsible for the antisymmetric scattering between states with wave vectors  $\vec{k}$  and  $\vec{k}'$  is<sup>13,14</sup>

$$\begin{aligned} \langle \vec{k}' \pm; \alpha | \mathcal{H}_2 | \vec{k} \pm; \alpha \rangle &= iC(\theta_{\vec{k}\vec{k}'})(\hat{k} \times \hat{k}') \cdot \hat{z} \sum_{n=1}^N e^{i(\vec{k} - \vec{k}') \cdot \vec{R}_n} \\ &\quad \times \langle \alpha | S_{nz} | \alpha \rangle, \end{aligned} \quad (6)$$

where  $C(\theta_{\vec{k}\vec{k}'})$  is an even function of the scattering angle  $\theta_{\vec{k}\vec{k}'}$ . This describes the scattering along the direction perpendicular to  $\vec{k}$  and to the magnetization for spin-conserving

transitions, and does not affect the position of the energy bands to first order in perturbation theory.

For the coupling between the orbital motion of the conduction electrons and the localized spins we write, as proposed by Maranzana,<sup>14</sup>

$$\mathcal{H}_2 = \frac{\mu_0 e g \mu_B \hbar}{4 \pi m^*} \sum_{n=1}^N \frac{\vec{S}_n \cdot \vec{L}_n}{|\vec{r} - \vec{R}_n|^3} \quad (e < 0, \mu_B > 0), \quad (7)$$

and

$$C(\theta_{\vec{k}\vec{k}'}^{\pm}) = \frac{\mu_0 e g \mu_B \hbar}{m^* V} \frac{1}{\cos^2 \theta_{\vec{k}\vec{k}'}^{\pm}}. \quad (8)$$

For the mechanism suggested by Kondo<sup>13</sup> to explain the anomalous Hall effect in gadolinium, which involves a virtual excited state with one electron less in the  $4f$  shell,

$$C(\theta_{\vec{k}\vec{k}'}^{\pm}) = \frac{\lambda V_1^2}{2S\Delta_- N}, \quad (9)$$

where  $\lambda$  is the spin-orbit radial integral for  $4f$  electrons in the  $4f^6$  configuration,  $V_1$  is the mixing matrix element between the  $l=1$  component of the plane wave factor  $e^{i\vec{k}\vec{r}}$  of the Bloch function (which is modulated by a function  $u_{\vec{k}}$  with the periodicity of the lattice and of pure  $d$  character around each Eu site) and a  $4f$  orbital, and  $\Delta_-$  is the minimum energy necessary to excite one electron from the  $4f^7$  configuration to the Fermi level.

The nonperiodic part ( $\mathcal{H}'_1$ ) of  $\mathcal{H}_1$ , obtained by replacing the  $z$  component of  $\vec{S}_n$ ,  $S_{nz}$ , by  $S_{nz} - \sigma$  in Eq. (2), and  $\mathcal{H}_2$  induce transitions between different Bloch states, the probability of which is given to lowest order by Fermi's golden rule as

$$P^{(2)}(\vec{k}s; \alpha | \vec{k}'s'; \alpha') = \frac{2\pi}{\hbar} \delta(\epsilon_{\vec{k}}^s - \epsilon_{\vec{k}'}^{s'}) \times |\langle \vec{k}'s'; \alpha' | \mathcal{H}'_1 + \mathcal{H}_2 | \vec{k}s; \alpha \rangle|^2. \quad (10)$$

The energy transfer between the conduction electrons and the spin system has been neglected (quasielastic or quasi-static approximation), which is justified as long as the typical excitation energy of the latter is smaller than the thermal energy,<sup>11</sup> as is certainly the case above  $T_c$ . The right-hand side of Eq. (10) contains four terms. The two cross products cancel due to the fact that the matrix elements of  $\mathcal{H}_2$  are imaginary. From the definitions (8) and (9) it is easy to see that the contribution from the square of the matrix element of  $\mathcal{H}_2$  is *a priori* irrelevant in the case of Maranzana's mechanism and contributes less than 1% to the total transition probability (10) if a physically reasonable value is used for the ratio  $V_1/\Delta_-$  in Kondo's model. Therefore we expect that the temperature and magnetic-field dependence of the resistivity is controlled entirely by the exchange interaction between the conduction electrons and the localized moments.

Two types of transition have to be considered, those without spin flip by

$$\begin{aligned} & \langle j\vec{k}'\pm; \alpha | \mathcal{H}'_1 | i\vec{k}\pm; \alpha \rangle \\ &= \mp \frac{1}{2N} \sum_{n=1}^N J_{\vec{k}'\vec{k}}^{ji} e^{i[\vec{k}-\vec{k}'-(\pi/a)\hat{i}+(\pi/a)\hat{j}]\cdot\vec{R}_n} \\ & \times \langle \alpha | (S_{nz} - \sigma) | \alpha \rangle \end{aligned} \quad (11a)$$

and those with spin flip by

$$\begin{aligned} & \langle j\vec{k}'\mp; \alpha \pm 1 | \mathcal{H}'_1 | i\vec{k}\pm; \alpha \rangle \\ &= -\frac{1}{2N} \sum_{n=1}^N J_{\vec{k}'\vec{k}}^{ji} e^{i[\vec{k}-\vec{k}'-(\pi/a)\hat{i}+(\pi/a)\hat{j}]\cdot\vec{R}_n} \\ & \times \langle \alpha \pm 1 | S_n^{\pm} | \alpha \rangle, \end{aligned} \quad (11b)$$

where we have introduced the spin-raising and lowering operators  $S_n^{\pm} = S_{nx} \pm iS_{ny}$  at the site  $\vec{R}_n$ , and

$$J_{\vec{k}'\vec{k}}^{ji} = N \langle j\vec{k}' | J(\vec{r}) | i\vec{k} \rangle. \quad (11c)$$

For intravalley transitions ( $i=j$ ), the momentum transfer is small, and we can set  $J_{\vec{k}\vec{k}'}^{ii}$  equal to  $J$  defined in Eq. (4) above. The short range of the exchange integral in real space implies that the matrix element for intervalley scattering will not be much reduced with respect to  $J$ . Fortunately, the short wavelength of the associated spin fluctuations and, in particular, the small range of scattering angles available for this process, allow us to neglect it. The same argument can be used to dismiss intervalley scattering in Eq. (6).

To lowest order, the transition probabilities associated with the matrix elements (11a) and (11b) are then given by

$$\begin{aligned} P^{(2)}(\vec{k}\pm; \alpha | \vec{k}'\pm; \alpha') &= \frac{2\pi}{\hbar} \delta(\epsilon_{\vec{k}}^{\pm} - \epsilon_{\vec{k}'}^{\pm}) \\ & \times \left( \frac{J}{2N} \right)^2 \sum_{n,n'} e^{[i(\vec{k}-\vec{k}')\cdot(\vec{R}_n - \vec{R}_{n'})]} \\ & \times \langle (S_{nz} - \sigma)(S_{n'z} - \sigma) \rangle \end{aligned} \quad (12a)$$

and

$$\begin{aligned} P^{(2)}(\vec{k}\pm; \alpha | \vec{k}'\mp; \alpha') &= \frac{2\pi}{\hbar} \delta(\epsilon_{\vec{k}}^{\pm} - \epsilon_{\vec{k}'}^{\mp}) \\ & \times \left( \frac{J}{2N} \right)^2 \sum_{n,n'} e^{[i(\vec{k}-\vec{k}')\cdot(\vec{R}_n - \vec{R}_{n'})]} \\ & \times \langle S_n^{\pm} S_{n'}^{\mp} \rangle. \end{aligned} \quad (12b)$$

Following Haas,<sup>9</sup> we express the spin-correlation functions appearing in Eqs. (12a), and (12b) in terms of the generalized susceptibility per unit volume

$$\chi^{ij}(\vec{q}) = \frac{1}{V} \frac{(g\mu_B)^2}{k_B T} \sum_{n,m} e^{[i\vec{q}\cdot(\vec{R}_n - \vec{R}_m)]} \times \{ \langle S_{ni} S_{mj} \rangle - \langle S_{ni} \rangle \times \langle S_{mj} \rangle \}, \quad (13)$$

where  $i, j = x, y, z$ . For a simple cubic (lattice constant  $a$ ) collinear ferromagnet, with one magnetic atom per unit cell,  $\chi^{ij}$  is diagonal and can be written as

$$\chi^i(\vec{q}) = [(\chi_h^i)^{-1} + Aq^2]^{-1} \quad (14)$$

for small values of  $\vec{q}$ , where  $\chi_h^i$  is the susceptibility per unit volume of a single domain in a homogeneous magnetic field and

$$A = \frac{V k_B T_C a^2}{2N(g\mu_B)^2 S(S+1)}. \quad (15)$$

The transport relaxation rate for a Bloch state  $|\vec{k}^\pm\rangle$ , with energy  $\epsilon_k^\pm$  is then given by<sup>9</sup>

$$\frac{1}{\tau_k^\pm} \equiv \frac{1}{\tau(\epsilon_k^\pm)} = \frac{2\pi}{\hbar} k_B T \left( \frac{J}{2N g \mu_B} \right)^2 V \sum_{\vec{k}'} [\chi^z(\vec{k}' - \vec{k}) \times \delta(\epsilon_k^\pm - \epsilon_{k'}^\pm) + 2\chi^x(\vec{k}' - \vec{k}) \delta(\epsilon_k^\pm - \epsilon_{k'}^\mp)]. \quad (16)$$

Inserting the explicit form of the susceptibilities and performing the sum over  $\vec{k}'$ , we finally obtain, for spin-disorder scattering,

$$P^{(3)}(\vec{k}^\pm; \alpha | \vec{k}'^\pm; \alpha) \approx \frac{2\pi}{\hbar} \delta(\epsilon_k^\pm - \epsilon_{k'}^\pm) \text{Re} \left[ \langle \vec{k}'^\pm; \alpha | \mathcal{H}_2 | \vec{k}^\pm; \alpha \rangle \sum_{\vec{k}'', s'', \alpha''} \frac{\langle \vec{k}^\pm; \alpha | \mathcal{H}_1 | \vec{k}'' s''; \alpha'' \rangle \langle \vec{k}'' s''; \alpha'' | \mathcal{H}_1 | \vec{k}'^\pm; \alpha \rangle}{\epsilon_k^\pm - \epsilon_{k''}^{s''} + i\delta} \right], \quad (22)$$

where the real part is derived by use of the identity

$$\frac{1}{\epsilon_k^s - \epsilon_{k''}^{s''} + i\delta} = \mathcal{P} \left( \frac{1}{\epsilon_k^s - \epsilon_{k''}^{s''}} \right) - i\pi \delta(\epsilon_k^s - \epsilon_{k''}^{s''}). \quad (23)$$

In contrast to Kondo and Maranzana, we allow for spin-flip exchange scattering to and from the summed-over intermediate states, but the inelasticity in energy has again been neglected. Inserting the appropriate matrix elements, we obtain

$$\frac{1}{\tau(\epsilon_k^\pm)} = \frac{1}{16\sqrt{2}\pi} \frac{\sqrt{m^*} k_B T}{\hbar^2 \sqrt{\epsilon_k^\pm}} \left( \frac{J}{N g \mu_B} \right)^2 V^2 \times \left[ \frac{1}{A} \ln \left( 1 + \frac{8m^* A}{\hbar^2} \chi_h^z \epsilon_k^\pm \right) + \frac{2}{A} \ln \left( \frac{1 + \frac{2m^* A}{\hbar^2} \chi_h^x (\epsilon_k^\pm + \epsilon_k^\mp + 2\sqrt{\epsilon_k^\pm \epsilon_k^\mp})}{1 + \frac{2m^* A}{\hbar^2} \chi_h^x (\epsilon_k^\pm + \epsilon_k^\mp - 2\sqrt{\epsilon_k^\pm \epsilon_k^\mp})} \right) \right]. \quad (17)$$

In the molecular-field approximation, we have<sup>9</sup>

$$\vec{M} = M_{\text{sat}} \hat{z} B_S(g\mu_B S | \vec{F} / k_B T), \quad (18)$$

where  $B_S$  is the Brillouin function for a spin  $S$  acted upon by the effective field

$$\vec{F} = \mu_0 \gamma \vec{M} + \vec{B}_a. \quad (19)$$

Here  $\gamma$  is the molecular field constant and  $\vec{B}_a$  is the applied external field, so that

$$\chi_h^x = \chi_h^y = M/B_a \quad (20)$$

and

$$\chi_h^z = \{ [M_{\text{sat}} (\partial B_S / \partial F)]^{-1} - \mu_0 \gamma \}^{-1}. \quad (21)$$

The antisymmetric scattering responsible for the observed anomalous Hall effect has its origin in the matrix element given in Eq. (6). For it to appear linearly in the transition probability, we need to compute the latter to third order in the matrix elements,<sup>13,14,16</sup> which leads to

$$P^{(3)}(\vec{k}^\pm; \alpha | \vec{k}'^\pm; \alpha) = \frac{2\pi}{\hbar} \left( \frac{J}{2N} \right)^2 C(\theta_{\vec{k}\vec{k}'}^{\pm}) \delta(\epsilon_k^\pm - \epsilon_{k'}^\pm) \times (\hat{k} \times \hat{k}') \cdot \hat{z} \times \sum_{\vec{k}'', s''} \delta(\epsilon_k^\pm - \epsilon_{k''}^{s''}) \times D_S^{(3)}(\vec{k}, \vec{k}', \vec{k}'') \quad (24)$$

with

$$D_S^{(3)}(\vec{k}, \vec{k}', \vec{k}'') = \sum_{n,p,q} e^{i[(\vec{k}-\vec{k}')\cdot\vec{R}_n + (\vec{k}''-\vec{k})\cdot\vec{R}_p + (\vec{k}'-\vec{k}'')\cdot\vec{R}_q]} \times [\langle S_{nz}(S_{pz}-\sigma)(S_{qz}-\sigma) \rangle + \langle S_{nz}S_p^\mp S_q^\pm \rangle]. \quad (25)$$

In the spirit of molecular field theory, we now assume that the sum over three-spin correlation functions can be limited to those terms in which  $n=p$  or  $n=q$ , and then make the following decoupling:

$$D_S^{(3)}(\vec{k}, \vec{k}', \vec{k}'') \approx \sigma \sum_{p,q} [e^{i(\vec{k}''-\vec{k}')\cdot(\vec{R}_p-\vec{R}_q)} + e^{i(\vec{k}''-\vec{k})\cdot(\vec{R}_p-\vec{R}_q)}] \times [\langle (S_{pz}-\sigma)(S_{qz}-\sigma) \rangle + \langle S_p^\mp S_q^\pm \rangle], \quad (26)$$

which, with the definition of the generalized susceptibility (13), leads to

$$D_S^{(3)}(\vec{k}, \vec{k}', \vec{k}'') = V \frac{k_B T}{(g\mu_B)^2} \sigma [\chi^z(\vec{k}''-\vec{k}') + \chi^z(\vec{k}''-\vec{k}) + 2\chi^x(\vec{k}''-\vec{k}') + 2\chi^x(\vec{k}''-\vec{k})]. \quad (27)$$

The sum over intermediate states in Eq. (24) is now identical to the one appearing in the expression for the transport relaxation rate of Eq. (16), with  $\epsilon_{\vec{k}''}^{\pm} = \epsilon_{\vec{k}''}^{\pm}$  or  $\epsilon_{\vec{k}''}^{\mp}$  for spin conserving or spin-flip transitions, respectively. This allows us to write the transition probability for skew scattering in the compact form

$$P^{(3)}(\vec{k}\pm; \alpha | \vec{k}'\pm; \alpha) = 2C(\theta_{\vec{k}\vec{k}'}^{\pm}) \delta(\epsilon_{\vec{k}}^{\pm} - \epsilon_{\vec{k}'}^{\pm}) \cdot (\hat{k} \times \hat{k}') \times \hat{z} \cdot \frac{1}{\tau(\epsilon_{\vec{k}}^{\pm})} \sigma, \quad (28)$$

where we have used the fact that the relaxation rate of a particular Bloch state only depends on its energy. Given an interaction with the above angular dependence, we can use the exact result derived by Fert<sup>17</sup> for the Hall resistivity  $\rho_H$  [his Eq. (15)], to define the relaxation rate for antisymmetric scattering

$$\frac{1}{\tau_{as}(\epsilon_{\vec{k}}^{\pm})} = \frac{V}{8\pi^3} \int d^3k' P^{(3)}(\vec{k}\pm; \alpha | \vec{k}'\pm; \alpha) \hat{k}' \cdot \hat{y} = \tilde{C}k \frac{1}{\tau(\epsilon_{\vec{k}}^{\pm})} \sigma, \quad (29)$$

where, for the interaction proposed by Maranzana<sup>14</sup>

$$\tilde{C}^M = \frac{\mu_0 e g \mu_B}{2\pi^2 \hbar} = 1.794 \times 10^{-15} \text{ m}. \quad (30)$$

For the mechanism, suggested by Kondo<sup>13</sup> to explain the anomalous Hall effect in gadolinium metal,

$$\tilde{C}^K = \frac{m^* \Omega_{\text{cell}} \lambda V_1^2}{6\pi^2 S \Delta_-^2 \hbar^2}, \quad (31)$$

where  $\Omega_{\text{cell}}$  is the volume of the unit cell.

In our comparison with experiment, the constant  $\tilde{C}$  in Eq. (29) will be treated as a free parameter.

## B. Experimental results and analysis

### 1. Temperature-dependent electrical resistivity in zero magnetic field

The temperature-dependent electrical resistivity arises from several scattering processes, which we shall, as usual, consider as independent (Matthiessen's rule). From the theory developed above we can calculate the conductivity of the coupled spin-up and spin-down charge carriers in the presence of spin-disorder scattering only according to

$$\sigma_{sd}^{\pm}(B_a, T) = -\frac{2e^2}{3m^*} \int_{-\infty}^{\infty} \tau_{sd}^{\pm}(\epsilon) (\epsilon - \epsilon_0^{\pm}) g^{\pm}(\epsilon) \frac{\partial f_0(\epsilon)}{\partial \epsilon} d\epsilon \quad (32)$$

with the Fermi function

$$f_0(\epsilon) = \frac{1}{1 + \exp\left(\frac{\epsilon - \zeta}{k_B T}\right)}, \quad (33)$$

where  $\zeta$  stands for the chemical potential. The density of states for each spin orientation is

$$g^{\pm}(\epsilon) = \frac{3}{4\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} (\epsilon - \epsilon_0^{\pm})^{1/2}. \quad (34)$$

The relaxation times  $\tau_{sd}^{\pm}(\epsilon) \equiv \tau(\epsilon_{\vec{k}}^{\pm})$  are given by Eq. (17). In the absence of a magnetic field and in the temperature range considered here, the system is unpolarized ( $\epsilon_0^+ = \epsilon_0^-$ ), and the relaxation time is the same for both spin orientations. We can then define the spin-disorder resistivity as

$$\rho_{sd}(0, T) = [\sigma_{sd}^+(0, T) + \sigma_{sd}^-(0, T)]^{-1}. \quad (35)$$

In order to calculate the contribution  $\rho_{ph}$  of the electron-phonon interaction to the resistivity, we use the model that was recently suggested by Mandrus and collaborators<sup>18</sup> for LaB<sub>6</sub>. The electrons are assumed to be scattered by localized low-frequency Einstein oscillators, corresponding to the almost independent motion of the rare-earth ions in their boron "cages," as well as by Debye-type phonons due to the collective motion of the boron framework. In a first step, we apply the model, described in detail in Ref. 18, to fit the resistivity data of YbB<sub>6</sub>.<sup>19</sup> In this compound, the Yb cations also adopt a divalent configuration but they carry no magnetic moment. We then renormalize the obtained Einstein frequency by the square root of the mass ratio between Yb and Eu, leading to  $\theta_E = 168$  K for EuB<sub>6</sub>. The Debye frequency ( $\theta_D = 1160$  K), to which the results are not sensitive

to start with, is left unchanged. Next, we have to account for the resistivity  $\rho_d$  arising from the scattering of the conduction electrons at point defects. We anticipate the charge-carrier density to be high enough to efficiently screen the latter and therefore, the corresponding relaxation rate can be considered as temperature independent. The total resistivity is then given by

$$\rho(0,T) = \rho_{sd}(0,T) + \rho_{ph}(0,T) + \rho_d(0,T) + \rho_{cont}, \quad (36)$$

where  $\rho_{cont}$  is a (small) contribution arising from nonideal electrical contacts to the sample, and which we assume to be independent of temperature and magnetic field.

In the next step we compare Eq. (36) with the measured temperature-dependent resistivity. To begin with, we postulate that the mobile charge carriers in the conduction band originate from the transfer of electrons from doubly and singly occupied levels of  $B_6$  vacancies. The existence of such defects has been invoked by Noack and Verhoeven<sup>20</sup> to explain their gravimetric data on zone refined  $LaB_6$ . Their formation energy has been shown to be substantially smaller than that of six widely separated B vacancies.<sup>21</sup> An excellent fit is obtained in the range  $40 \text{ K} \leq T \leq 100 \text{ K}$  with a constant carrier concentration of  $1.4 \times 10^{25} \text{ m}^{-3}$  or  $10^{-3}$ /unit cell, which corresponds to a Fermi energy  $E_F$  of 54 meV. At elevated temperatures, the experimental data suggest that electrons from a narrow “band” of defect states which, for reasons that are elucidated below, we associate with compensating ionized acceptors in the form of Eu vacancies, start to populate the conduction band. The experimental data are well reproduced if we assume a concentration of  $6 \times 10^{25} \text{ m}^{-3}$  defect levels, with a Lorentzian energy distribution centered at 19 meV below the conduction band edge (i.e., 73 meV below  $E_F$ ) and a full width at half maximum of 9 meV. Finally, our fit requires the density of mobile charge carriers to increase by 40% as the temperature is reduced from 40 K to 22.5 K. This increase can be explained by an early onset of magnetic short range order,<sup>22</sup> nucleated by the presence of defects, which locally reduces the activation energy of the donor states. The different components of the resistivity, their sum, and the measured curve are displayed in Fig. 1. The experimental  $\rho(T)$  is in excellent agreement with previous data reported by Weill and collaborators.<sup>23</sup> However, both these data sets yield systematically higher values of the resistivity than those observed by other groups<sup>24–27</sup> except one<sup>28</sup> which provides data only up to 90 K. At room temperature we find (in units of  $10^{-6} \Omega \text{ m}$ ) 11.8, compared to 6.1,<sup>24</sup> 8.0,<sup>25</sup> 3.2,<sup>26</sup> and 7.3.<sup>27</sup> This again demonstrates the sensitivity of the system to the growth conditions, as do the residual resistivity data displayed in Fig. 1 of Ref. 6.

In contrast to earlier work,<sup>26</sup> where the contribution from electron-phonon scattering to the room temperature resistivity was estimated to be less than 3%, our analysis shows that this mechanism actually dominates above 125 K and is responsible for over 60% of the total resistivity at room temperature. This contribution would be even more dominant if it was not for the thermally activated increase of mobile charge carriers with increasing temperature mentioned ear-

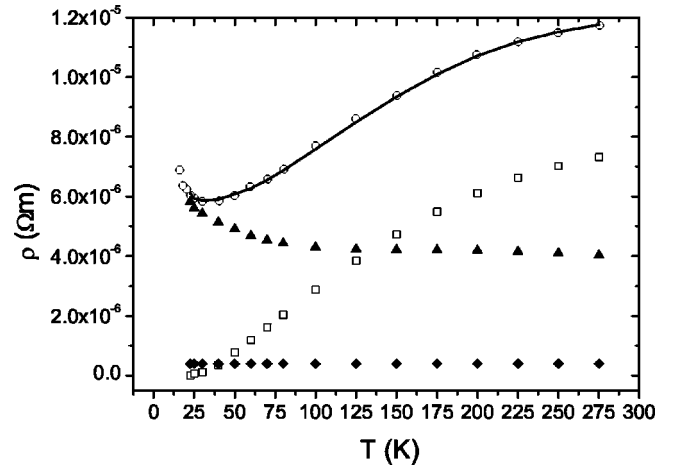


FIG. 1. The total measured resistivity  $\rho$  of  $\text{EuB}_6$  is represented by open circles. The calculated contributions due to scattering by phonons and magnetic excitations are shown by open squares and closed triangles, respectively. The closed diamonds represent the combined contribution to the resistivity of the scattering by point defects and of the nonideal contacts. The solid line represents the total calculated resistivity in zero external field above 20 K.

lier. Due to the small size of  $\rho_d + \rho_{cont}$ , an unambiguous estimate of the contact term is not possible at this stage and requires the analysis of the magnetoresistance given below. The variation of the charge-carrier density with temperature is summarized in Fig. 2.

## 2. Magnetoresistance

The magnetization of our sample as a function of the applied magnetic field is displayed for a large number of temperatures in Fig. 3, which also shows the results of a fit using Eq. (18) to all measured temperatures and fields above 30 K. The latter yields a saturation magnetization of  $(8.83 \pm 0.04) \times 10^5 \text{ A/m}$ , in excellent agreement with the value of  $8.86 \times 10^5 \text{ A/m}$  expected for divalent europium, and an effective molecular field parameter  $\gamma = 5.15 \pm 0.05$ . Besides

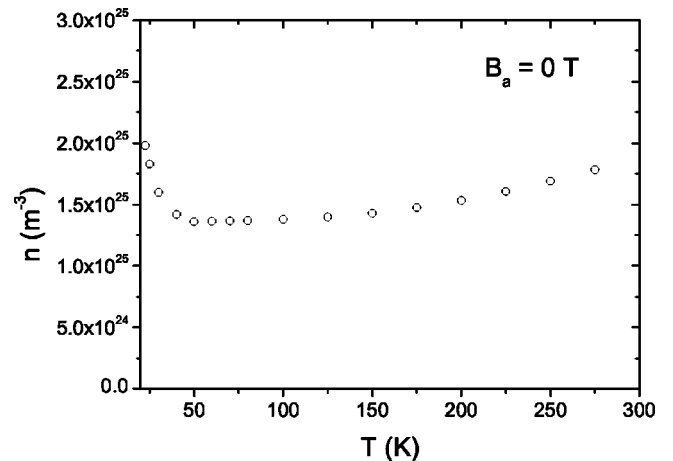


FIG. 2. Itinerant carrier density  $n(T)$  in  $\text{EuB}_6$  at high temperatures, obtained from the separation of the total resistivity into a magnetic, a phononic, and an impurity contribution (see Fig. 1).

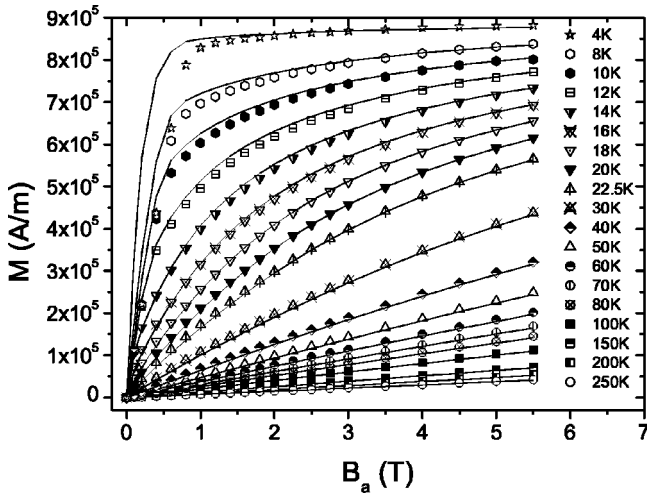


FIG. 3. Bulk magnetization  $M$  of  $\text{EuB}_6$  as a function of applied magnetic field  $B_a$  oriented perpendicularly to the platelet-shaped sample. All data for temperatures above 30 K, where fitted according to Eq. (18), yielding the parameters  $M_{\text{sat}}$  and  $\gamma$ . The solid lines represent the mean-field calculations for all temperatures using these parameters. Good agreement between this type of calculation and experiment prevails to even lower temperatures.

the Weiss field,  $\gamma$  contains the Lorentz field [ $\gamma_L = (1/3)$ ], negligible in higher- $T_C$  materials, and the demagnetizing field ( $\gamma_D \approx -0.93$  for our geometry). The Curie temperature of an infinite size bulk sample is determined by the first two terms and amounts to 13.6 K, close to the temperature at which neutron-scattering experiments<sup>29</sup> reveal the onset of spontaneous magnetic order.

The parameters also allow to calculate the longitudinal and transverse susceptibilities using Eqs. (21) and (20), respectively, as well as the shift of the bottoms of the spin-up and spin-down conduction bands, induced by the nonzero magnetization, via Eq. (5). The latter leads to a redistribution of charge carriers between the two bands which, in turn, requires an adjustment of the chemical potential with respect to the band minima. The Eu-vacancy levels will also, to a lesser extent, be affected by the magnetization. The spin-down states will rise in energy and progressively empty themselves into the (spin-up) conduction band. At some temperature-dependent value of the field, the latter will merge with the spin-up Eu-vacancy states. Due to the Pauli principle, the transport properties will not be affected, however.

The resistivity may now be calculated as follows. For all values of the applied field and temperature, we define two average relaxation rates

$$\frac{1}{\tau_{sd}^{\pm}} = \frac{1}{\sigma_{sd}^{\pm}(B_a, T)} \frac{n^{\pm} e^2}{m^*} \quad (37)$$

due to spin-disorder scattering. According to the model of Mandrus *et al.*<sup>18</sup> the electron-phonon relaxation rate is proportional to the Fermi velocity and hence, because  $v_F \sim n^{1/3}$ , we can write

$$\frac{1}{\tau_{ph}^{\pm}} = \left( \frac{n^{\pm}}{n/2} \right)^{1/3} \frac{1}{\tau_{ph}^0} = \frac{e^2}{m^*} n \left( \frac{n^{\pm}}{n/2} \right)^{1/3} \rho_{ph}(0, T). \quad (38)$$

Finally, we assume that the (weak) scattering by point defects is field independent, which leads to the total average relaxation rate

$$\frac{1}{\tau^{\pm}} = \frac{e^2}{m^*} \left[ n^{\pm} \frac{1}{\sigma_{sd}^{\pm}(B_a, T)} + n \left( \frac{2n^{\pm}}{n} \right)^{1/3} \rho_{ph}(0, T) + n \rho_d(0, T) \right], \quad (39)$$

and to the total resistivity in the presence of a magnetic field

$$\rho(B_a, T) = \frac{m^*}{e^2} (n^+ \bar{\tau}^+ + n^- \bar{\tau}^-)^{-1} + \rho_{\text{cont}}. \quad (40)$$

In passing we note a spin polarization of the itinerant electrons, arising from a redistribution of the charge carriers between the spin-up and spin-down bands, resulting from the opposite shifts of the band edges  $\epsilon_0^+$  and  $\epsilon_0^-$  described by Eq. (5). These shifts alone leave the density of mobile charge carriers constant but the negative shift of the majority band leads to a transfer of carriers from localized defect to itinerant band states.

The free parameters in the model are the exchange coupling constant  $J$ , the effective mass  $m^*$ , the contact resistivity  $\rho_{\text{cont}}$ , and the charge-carrier density  $n_{\text{tot}}(B_a)$ . The best agreement with experiment is obtained for  $J = 0.18$  eV,  $m^* = 0.22m_e$ , where  $m_e$  is the free-electron mass, and  $\rho_{\text{cont}} = 1.5 \times 10^{-7} \Omega \text{ m}$ . A 10% (correlated) variation of the parameters still produces reasonable results. Our optimum value for the exchange coupling constant is very close to the one quoted by Rys *et al.*<sup>8</sup> for divalent europium (0.188 eV) and our value for  $m^*$  compares well with the density of states mass  $m_{\text{DOS}} = 0.26m_e$  yielded by the LSDA band-structure calculation.<sup>4</sup> The absolute values of the carrier densities  $n_{\pm}(B_a)$  depend strongly on  $J$  and  $m^*$ , but their relative changes are identical for all parameters.

Figure 4 displays the measured curves for  $\rho(B_a, T)$  at 22.5, 40, 60, 80, 125, and 175 K. The solid lines represent the calculations at the corresponding temperatures and fields. We note a perfect agreement at temperatures above 60 K. At 22.5 K and fields less than  $\sim 2$  T, strong polarization effects induce a substantial variation of  $n(B_a)$  which is difficult to model. Nevertheless, the calculated curve reproduces the measured results to within 5%. For stronger magnetic fields the measured curve for  $\rho(B_a)$  decreases more slowly with increasing magnetic field, reflecting a further reduction of the spin-disorder scattering and an increase of the charge-carrier density. Eventually,  $\rho(B_a)$  flattens out and subsequently increases slightly towards the highest fields, which we interpret as the onset of conductivity through a second band, described in more detail in the section on the low-temperature

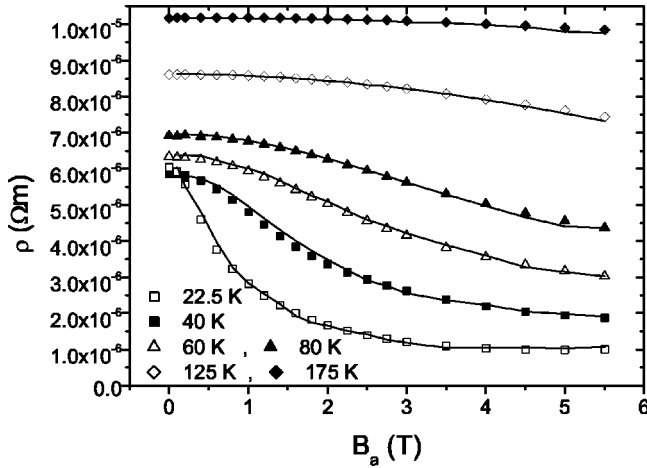
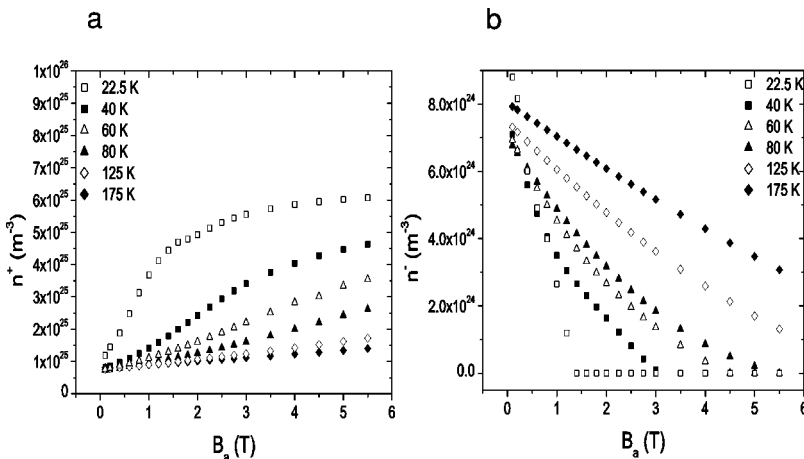


FIG. 4. Magnetoconductivity of  $\text{EuB}_6$  at 22.5, 40, 60, 80, 125, and 175 K, between 0 and 5.5 T. The solid lines are the results of the resistivity calculations described in the text.

transport. The charge carriers in this second band are holes with a concentration increasing from 0 at 4 T to  $n_h = 0.8 \times 10^{25} \text{ m}^{-3}$  at 5.5 T.

In Figs. 5(a) and 5(b) we display the electron densities  $n^+$  and  $n^-$  in the spin-up and spin-down band, respectively, for the same temperatures and fields for which  $\rho(B_a)$  was calculated. With decreasing temperature, the polarization effects lead to a stronger enhancement of  $n^+$  and a corresponding reduction of  $n^-$  with increasing field. At 60 K  $n^-$  vanishes at  $\approx 4.5$  T, leaving a fully polarized conduction band. At 40 K,  $n^-$  vanishes at 3 T and at 22.5 K already at 1.4 T. As mentioned before, an increasing concentration of holes has to be introduced below 40 K in order to explain the high-field ( $B_a > 4$  T) data. The only plausible mechanism for this to happen is that, e.g., at 22.5 K and 4 T, the top of the spin moment up valence band which, according to the calculation of Massidda *et al.*<sup>4</sup> should experience an (upward) shift of the order of 15% of that of the bottom of the conduction band, touches the Fermi level  $E_F$ . Note that this is not in contradiction with the existence of ionized (i.e., occupied by electrons) acceptor states below  $E_F$ .



### 3. Hall effect

In a magnetic conductor, the Hall resistance consists of two contributions, namely, the ordinary part  $\rho_H^{\text{ord}}$ , due to the Lorentz force  $e\vec{v} \times \vec{B}$  acting on the electrons, and the anomalous part  $\rho_H^{\text{mag}}$ , which results from the antisymmetric scattering of itinerant charge carriers by the disordered local moments on the magnetic ions.<sup>30</sup> The spin-flip exchange scattering mixes the states of the spin-up and spin-down conduction bands, which can therefore be considered as a single entity. Therefore the ordinary Hall resistivity is related to the total density of mobile charge carriers,  $n_{\text{tot}}$  by the usual relation

$$\rho_H^{\text{ord}} = -\frac{1}{n_{\text{tot}}e}B \quad (41)$$

with  $\vec{B} = \vec{B}_a + \mu_0(1 - \gamma_D)\vec{M}$ .

In Fig. 6 we display the measured Hall resistivity  $\rho_H$  as a function of applied field for 22.5, 60, 125, and 275 K, together with  $\rho_H^{\text{ord}}$  computed with the charge-carrier densities obtained from the fit to the magnetoconductivity data. The difference between the measured Hall resistivity and  $\rho_H^{\text{ord}}$  is largest at low temperatures and in small fields, where the spin-up and spin-down carrier densities are most sensitive to fluctuations in the magnetization (see Fig. 5).

We attempted to model this difference, which we interpret as the anomalous Hall resistivity  $\rho_H^{\text{mag}}$ , using the relaxation rate for antisymmetric scattering given by Eq. (29). Treating  $\tilde{C}$  as a free parameter in a fit to  $\rho_H^{\text{mag}}$  with  $\rho_H^{\text{mag}} = (\sigma_H^{\text{mag},+} + \sigma_H^{\text{mag},-})^{-1}$ , and inserting the Hall conductivities obtained from Eq. (32) with  $\tau_{sd}$  replaced by  $\tau_{as}$ , yields the curves shown in Fig. 7 and the optimum value  $\tilde{C} \approx (6.6 \pm 0.5) \times 10^{-11} \text{ m}$ , exceeding that of  $\tilde{C}^M$  [Eq. (30)] by more than four orders of magnitude. Using the value of  $m^*$  obtained from our fit to the magnetoconductivity, the spin-orbit coupling constant  $\lambda = 164 \text{ meV}$  for the intermediate  $4f^6$  configuration<sup>31</sup> and the lattice constant  $a = 4.185 \text{ \AA}$ , we can write the corresponding coefficient for the Kondo mechanism as

FIG. 5. The charge-carrier concentrations  $n^+(B_a)$  (a) and  $n^-(B_a)$  (b) in the spin moment up and spin moment down band, respectively, at 22.5, 40, 60, 80, 125, and 175 K between 0 and 5.5 T. Note the different scales of the y axis.



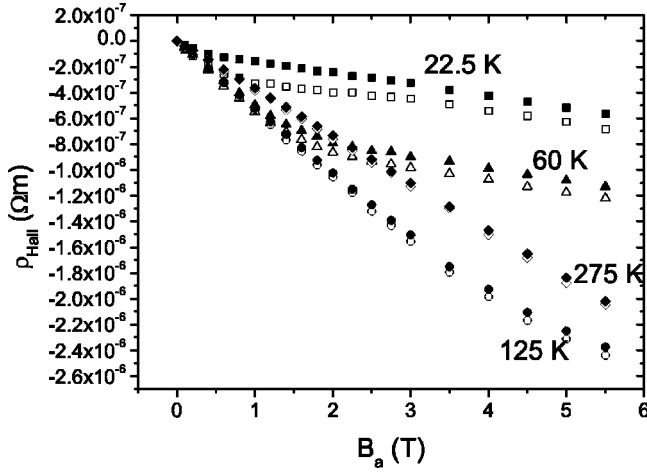


FIG. 6. Measured Hall resistivities  $\rho_{\text{Hall}}(B_a)$  and calculated ordinary Hall resistivities  $\rho_H^{\text{ord}}$  of  $\text{EuB}_6$  at 22.5, 60, 125, and 275 K between 0 and 5.5 T. The empty symbols show  $\rho_{\text{Hall}}(B_a)$ , the full symbols display  $\rho_H^{\text{ord}}$ .

$$\tilde{C}^K = 1.77 \times 10^{-13} \frac{V_1^2}{\Delta_-^2} \text{ m}. \quad (42)$$

For  $\tilde{C}^K$  to adopt the optimum value obtained from the fit to  $\rho_H - \rho_H^{\text{ord}}$  would require the ratio  $V_1/\Delta_-$  to be of the order of 20, which is utterly unrealistic. According to x-ray photoemission experiments,<sup>32</sup> the lower bound on  $\Delta_-$  ( $^7\text{F}_0$  final state) is  $\sim 0.7$  eV and  $V_1$  is expected to be smaller. It appears that discrepancies of that order are the rule for systems with half-filled  $4f$  shells in their ground state, such as gadolinium and Gd compounds.<sup>13,33</sup>

#### IV. LOW-TEMPERATURE TRANSPORT

At temperatures below 8 K, electron-phonon scattering is negligibly small, and the only contributions to the resistivity

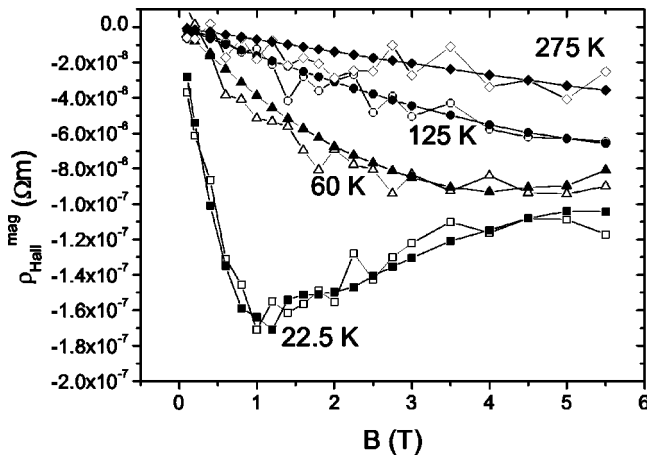


FIG. 7. Calculated and experimentally derived anomalous Hall resistivities  $\rho_H^{\text{mag}}(B_a)$  of  $\text{EuB}_6$  at 22.5, 60, 125, and 275 K between 0 and 5.5 T. The empty symbols show the difference between the measured Hall resistivity  $\rho_H$  and the corresponding calculated ordinary contribution  $\rho_H^{\text{ord}}$ . The full symbols display the calculated anomalous Hall resistivities  $\rho_H^{\text{mag}}$ .

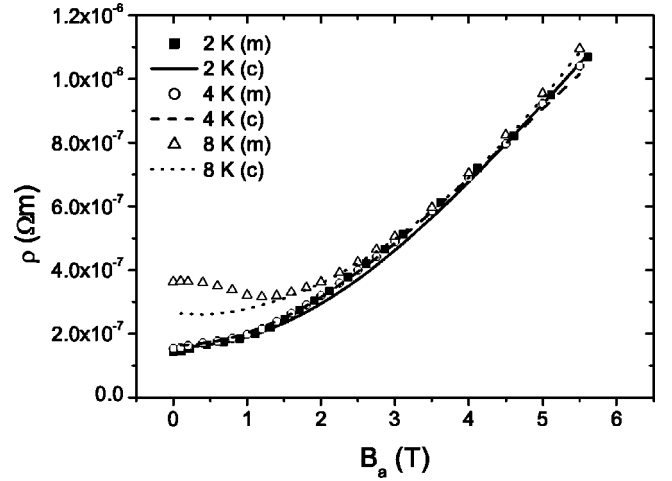


FIG. 8. The measured (*m*) magnetoresistivity data  $\rho(B_a)$  for  $\text{EuB}_6$  are displayed for 2, 4, and 8 K between 0 and 5.5 T. The calculated (*c*) curves are obtained for the corresponding temperatures, using the two-band model captured by Eqs. (43a) and (43b).

are  $\rho_{sd}$ ,  $\rho_d$ , and  $\rho_{\text{cont}}$ . In Figs. 8 and 9, the data for the magnetoresistance and the Hall resistance are plotted for 2, 4, and 8 K. At 2 K,  $\rho(B_a)$  increases by a factor of  $\approx 7$  between 0 and 5.5 T. In fields exceeding 1.5 T,  $\rho(B_a)$  is nearly quadratic in  $B_a$  for all three temperatures. This observation strongly suggests that two bands with oppositely charged carriers participate in the conduction of electrical current. For  $B_a > 1.5$  T, we therefore use a standard two-band model<sup>34</sup> to simultaneously describe  $\rho_H(B_a)$  and  $\rho(B_a)$ . This leads to

$$R = \frac{R_1 \rho_2^2 + R_2 \rho_1^2 + R_1 R_2 (R_1 + R_2) B_a^2}{(\rho_1 + \rho_2)^2 + (R_1 + R_2)^2 B_a^2} \quad (43a)$$

and

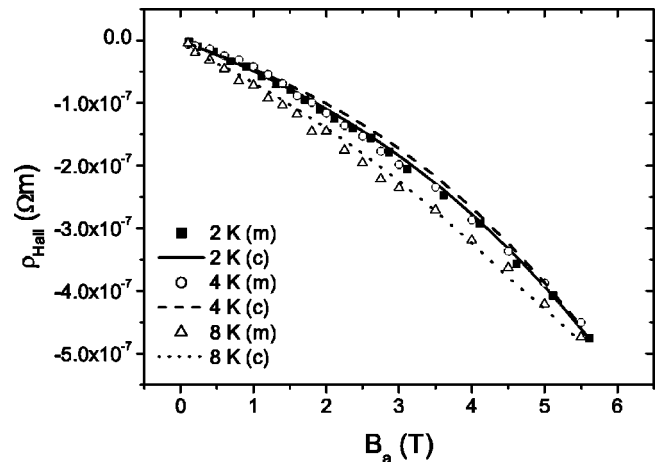


FIG. 9. The measured (*m*) Hall resistivity data  $\rho_H(B_a)$  for  $\text{EuB}_6$  are displayed for 2, 4, and 8 K between 0 and 5.5 T. The calculated (*c*) curves are again obtained, using the two-band model captured by Eqs. (43a) and (43b).

$$\rho = \frac{\rho_1 \rho_2 (\rho_1 + \rho_2) + (\rho_1 R_2^2 + \rho_2 R_1^2) B_a^2}{(\rho_1 + \rho_2)^2 + (R_1 + R_2)^2 B_a^2} + \rho_{\text{cont}}, \quad (43b)$$

where  $R_1$ ,  $R_2$ ,  $\rho_1$ , and  $\rho_2$  depend on temperature and on the applied field. The Hall “constant”  $R$  is the proportionality factor between  $\rho_H(B_a)$  and  $B_a$ ;  $R_1$  and  $R_2$  are the Hall “constants” for the conduction and the valence band, respectively.

At 8 K and in zero external field, the ordered Eu moment is of equal magnitude<sup>29</sup> as the net moment per Eu ion in the field direction at 22.5 K and  $B_a = 5.5$  T. Hence we expect to find the same concentration of electrons  $n_e \approx 6.1 \times 10^{25} \text{ m}^{-3}$  in the (fully polarized) conduction band and the same value of  $R_1(8 \text{ K}, 0 \text{ T}) \approx -1.0 \cdot 10^{-7} \text{ m}^3 \text{ A}^{-1} \text{ s}^{-1}$  in both cases. Similarly  $n_h \approx 0.8 \times 10^{25} \text{ m}^{-3}$  and  $R_2(8 \text{ K}, 0 \text{ T}) \approx 7.7 \times 10^{-7} \text{ m}^3 \text{ A}^{-1} \text{ s}^{-1}$ . We determine  $\rho_1$  and  $\rho_2$  under the same conditions as follows. First we note [Fig. (8)] that the contribution from spin-disorder scattering to the total resistivity is negligibly small for  $B_a \geq 1.5$  T. For applied fields in excess of this value  $\rho_1$  ( $\rho_2$ ) is therefore entirely due to the scattering of electrons (holes) by point defects, and is proportional to the density of electrons (holes), with no explicit dependence on  $B_a$ . This allows us to extrapolate this contribution, which we call  $\rho_{1d}$  ( $\rho_{2d}$ ), to zero applied field as follows:

$$\begin{aligned} \rho_{1d}(8 \text{ K}, 0 \text{ T}) &= \rho_{1d}(22.5 \text{ K}, 5.5 \text{ T}) \\ &= \frac{n_e(22.5 \text{ K}, 0 \text{ T})}{n_e(22.5 \text{ K}, 5.5 \text{ T})} \rho_{1d}(22.5 \text{ K}, 0 \text{ T}) \\ &\approx 0.66 \times 10^{-7} \Omega \text{ m}, \end{aligned} \quad (44)$$

where the carrier densities can be read off Fig. 5, and  $\rho_{1d}(22.5 \text{ K}, 0 \text{ T})$  is obtained from Fig. 1 and  $\rho_{\text{cont}}$  determined in the preceding section. From the two-band model and in the absence of spin-disorder scattering it follows that  $\rho_{2d}(8 \text{ K}, 0 \text{ T}) \approx 1.44 \times 10^{-6} \Omega \text{ m}$ . Considering the ratio of the effective masses and the carrier concentrations for the two bands, we find that the relaxation time of the holes is approximately three times shorter than that of the electrons. Enhancing the applied field from 0 to 5.5 T induces a monotonous enhancement of the ordered Eu moment and thus the magnetization. This in turn enhances the overlap between the valence band and the conduction as well as the donor spin-up bands, leading to a net increase in the density of mobile charge carriers. From the fit of our experimental data to Eqs. (43a) and (43b) for  $B_a \geq 1.5$  T we obtain  $n_e = 6.7 \times 10^{25} \text{ m}^{-3}$  and  $n_h = 6.1 \times 10^{25} \text{ m}^{-3}$  at magnetic saturation. The growth rate is roughly proportional to  $(M/M_{\text{sat}})^{3/2}$ , as expected for parabolic bands. The residual spin disorder resistivity in zero field amounts to less than  $1 \times 10^{-7} \Omega \text{ m}$  [see Fig. 8].

Below 5 K the elementary excitations of the system of magnetic Eu ions are spin waves.<sup>29</sup> From a comparison of the zero-field resistivities at 2 and 4 K we see that the scattering of the charge carriers by these collective modes, which should be proportional to  $T^2$ , can be neglected. The field dependence of the (Hall) resistivity at these two temperatures

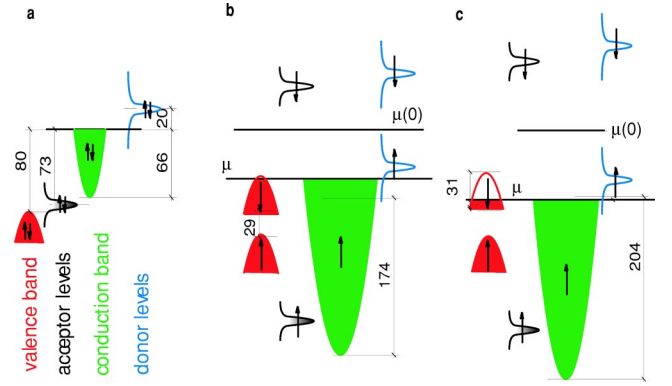


FIG. 10. (Color online) Schematic electronic excitation spectrum of  $\text{EuB}_6$  around the chemical potential  $\mu$  at  $T=22.5$  K. A possible arrangement of the conduction band, the valence band, an acceptor, and a donor defect band is plotted for (a)  $B_a=0$  T, (b)  $B_a=4$  T, (c)  $B_a=5.5$  T. From left to right in each panel: valence band, acceptor levels (cation vacancies), conduction band, donor levels ( $\text{B}_6$  vacancies). All energies are given in meV. The up arrows and down arrows denote the spin moment up and spin moment down subbands, respectively,  $\mu(0)$  is the chemical potential for  $B_a=0$  T, whereas  $\mu$  denotes the chemical potential at the corresponding fields. The distribution of the charge carriers over the four different bands is explained in the text. Note that in (b) and (c) the conduction subband for the down moment lies far above the chemical potential and is thus irrelevant for our purposes.

is again well reproduced by the two-band model, on which we have imposed the constraint that the resulting values for  $R_{1,2}$  and  $\rho_{1,2}$  at full magnetization are the same as at 8 K.

Our low-temperature magnetoresistance data compare well with those of Süllow *et al.*<sup>3</sup> In particular, we observe the same qualitative differences at low fields between  $\rho(H)$  at 2 K, 4 K (4.9 in Ref. 3) and 8 K (10 K in Ref. 3). At higher temperatures the spontaneous magnetization is much lower than the saturation value<sup>29</sup> and hence, in zero magnetic field, the spin-disorder scattering is significant. It is, however, suppressed by a weak external magnetic field.<sup>3</sup>

## V. DISCUSSION

In this paper we offer a consistent, quantitative description of the magnetoresistance and the Hall effect in  $\text{EuB}_6$  over a wide range of temperatures above and below the magnetic phase transition. From our analysis, the following picture of the electronic structure of this compound emerges. For  $T > 20$  K and no applied magnetic field,  $\text{EuB}_6$  is a heavily (self-) doped, strongly compensated  $n$ -type semiconductor. The donors are  $\text{B}_6$  vacancies, whose energy levels form a narrow “band” centered above the chemical potential, and possibly trivalent impurities, which we have neglected. The acceptors are cation vacancies, always present in the hexaborides, whose energy levels also form a narrow “band” just above the top of the valence band [Fig. 10(a)]. At 22.5 K, the intrinsic band gap is of the order of 14 meV and the chemical potential lies  $\sim 66$  meV above the bottom of the conduction band. Upon application of a magnetic field, the Eu ions acquire a net moment in the field direction. The

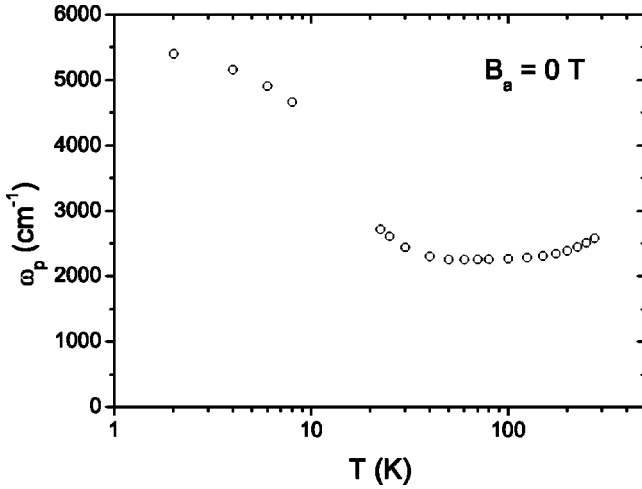


FIG. 11. Bare plasma frequency  $\omega_p$  of  $\text{EuB}_6$ , obtained from the calculated itinerant charge-carrier densities, vs temperature in zero magnetic field.  $\omega_p$  is calculated using Eq. (45) and the optical masses provided by the band-structure calculations ( $m_e^{\text{opt}} = 0.24m_e$ ,  $m_h^{\text{opt}} = 0.29m_e$ ).

latter couples to the conduction electrons through the exchange Hamiltonian  $\mathcal{H}_1$ , leading to a splitting of the conduction band proportional to the magnetization in first order. The acceptor levels, the wave functions of which are mainly composed of  $d_{z^2}$  orbitals reaching out from the neighboring cations, suffer a splitting of similar size, while that of the donor levels and especially that of the valence band, which both couple to the Eu moments only indirectly through hybridization with the cation's  $d$  orbitals, will be smaller.<sup>39</sup> These splittings lead to a redistribution of the charge carriers between the different bands and, in our model, at a temperature-dependent critical value of the applied field, e.g., 1.4 T at 22.5 K, the spin-down conduction band has emptied itself completely. At that point, the magnetization has reached only 25% of its saturation value. As the applied field and the magnetization are further enhanced, the top of the spin-down valence band moves closer to the self-consistently determined chemical potential [Fig. 10(b)], until it crosses it. At 5.5 T ( $M/M_{\text{sat}} \approx 0.65$ ) the situation is that of Fig. 10(c). Once the saturation magnetization has been reached, the carrier densities in the valence and the conduction band stay constant.

This picture is consistent with the observation of two ellipsoidal pockets in de Haas–van Alphen (dHvA) and Shubnikov–de Haas experiments, performed at fields above 5 T.<sup>6,35</sup> It also offers a natural explanation for the weak temperature dependence of the dHvA frequencies, even across  $T_C$ ,<sup>6</sup> since these are only affected by deviations of the  $4f$ -electron based magnetization from its saturation value. In view of the sensitivity of the system to defects, our carrier concentrations are in very reasonable agreement with the ones quoted in Refs. 6 and 35.

A further test of our interpretation is provided by the reflectivity experiments of Degiorgi and collaborators.<sup>2,36</sup> In Fig. 11 we display the bare plasma frequency

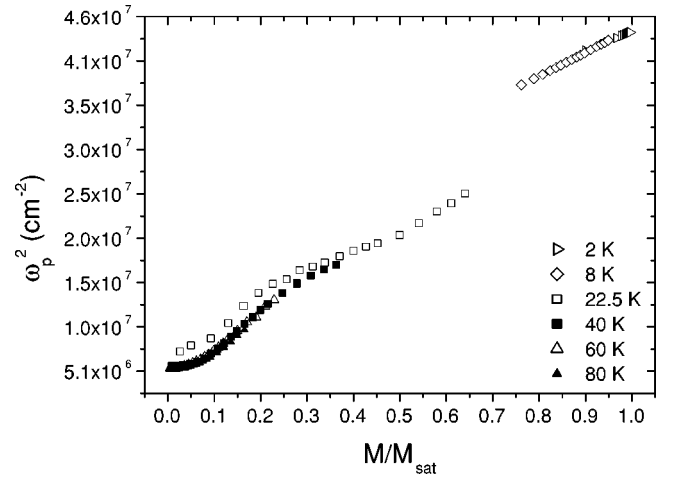


FIG. 12. Squared bare plasma frequency  $\omega_p^2$  of  $\text{EuB}_6$  vs the relative bulk magnetization  $M/M_{\text{sat}}$  at 2, 8, 22.5, 40, 60, and 80 K.  $\omega_p$  is calculated using Eq. (45) and the optical masses provided by the band-structure calculations ( $m_e^{\text{opt}} = 0.24m_e$ ,  $m_h^{\text{opt}} = 0.29m_e$ ).

$$\omega_p = \left[ \frac{e^2}{\epsilon_0} \left( \frac{n_e}{m_e^{\text{opt}}} + \frac{n_h}{m_h^{\text{opt}}} \right) \right]^{1/2} \quad (45)$$

as a function of temperature in zero field, calculated with the carrier densities obtained from our fits and the optical masses provided by the band-structure calculations of Ref. 4 ( $m_e^{\text{opt}} = 0.24m_e$ ,  $m_h^{\text{opt}} = 0.29m_e$ ). Our results compare well with the data of Ref. 2. In particular, we reproduce, even quantitatively, the steep rise of  $\omega_p$  below  $T_C$ . The decrease of the computed plasma frequency at temperatures between 300 K and 100 K is consistent with the observed red shift of the plasma edge in Ref. 2.

Figure 12 shows the dependence of the plasma frequency on magnetization obtained from our model. In Ref. 36,  $\omega_p^2$  was found to be proportional to  $M$  for  $1.6 \text{ K} \leq T \leq 35 \text{ K}$  and  $0 \text{ T} \leq B_a \leq 7 \text{ T}$ . Again, our results are compatible with this behavior, but suggest that the relation between the two quantities may be more complex.

Finally we compare our model with the ARPES and bulk-sensitive XAS and SXE data of Ref. 5, which were obtained in the temperature range between 20 and 30 K. The existence of an  $X$ -point electron pocket was assumed *a priori* in our theoretical ansatz, relying on the validity of these experimental results. The authors of Ref. 5 attribute the feature labeled “band 1” in their paper to the emission from the valence band. The fact that its dispersion is much weaker in  $\text{EuB}_6$  than in  $\text{CaB}_6$  and  $\text{SrB}_6$ , and the value of its binding energy of  $\sim 1.2 \text{ eV}$ , leads us to interpret it as an emission from the Eu  $4f$  shell. According to our model, the emission from the valence band should start at a binding energy of  $\sim 0.1 \text{ eV}$ , which is not seen in ARPES. This may be due to the fact that the exposed [100] face consists of metal atoms only and that the electrons, originating from the boron network, cannot escape from the solid at the given photon energies. Another complication is the observed time-dependent surface relaxation.<sup>5</sup> The SXE and XAS data are consistent with our interpretation of the ARPES data.

## VI. CONCLUSION

Although “real”  $\text{EuB}_6$  is a heavily doped, strongly compensated, and therefore very disordered magnetic semiconductor, many of its properties can be satisfactorily described by a relatively simple model, taking into account the two main intrinsic sources of imperfections, namely, Eu and  $\text{B}_6$  vacancies. Our microscopic treatment above  $T_C$  is limited to the range of temperatures where mean-field theory can be used to describe the magnetic properties of the compound. We expect the behavior around  $T_C$  (and the critical temperature itself) to be sample dependent, as the (Ruderman-Kittel-Kasuya-Yosida) coupling between magnetic ions is mediated by the conduction electrons whose concentration is a function of the magnetization.

The electronic transport in the temperature regime around the phase transition was carefully investigated by Süllow *et al.*<sup>3</sup> They interpreted their data to indicate the formation of small magnetic polarons, growing in size with increasing magnetization, as was previously suggested by Nyhus *et al.*<sup>22</sup> The eventual overlap of these polarons is claimed to lead to the sudden metallization of their sample at 15.5 K and the bulk Curie temperature is identified at 12.6 K. Their interpretation is based on the observation of two field sensitive modes in the Raman spectrum of this compound.<sup>22</sup> The symmetry of these modes as well as their temperature and field dependences are compatible with this interpretation. Our data do not contradict this view, but they show that below 8 K and above 22.5 K, a single-particle type picture provides a satisfactory description of the magnetoresistance of  $\text{EuB}_6$ .

What is still missing is a plausible mechanism leading to the correct order of magnitude for the anomalous Hall resistivity in this and the other compounds formed by rare-earth

ions with a half-filled  $4f$  shell. In our opinion the order of magnitude discrepancy between theory and experiment with respect to the anomalous Hall effect is not caused by underestimating the mixing matrix element  $V_1$ , as this would reflect itself in the resistivity as well. It must therefore be connected with the multiplicity of the intermediate states which can be coupled by the spin-orbit interaction. The lowest energy term for the  $4f^6$  configuration is characterized by  $L=3$  and  $S=3$ , with a degeneracy of 49 in the absence of spin-orbit coupling. Whereas the unit operator, relevant for the resistivity, only has diagonal matrix elements, the spin-orbit operator, which splits the term into seven multiplet levels  $J=0,1,\dots,6$ , has matrix elements between states satisfying the selection rule  $\Delta J_z=0,\pm 1$ , within every subspace corresponding to a given value of  $J$ . This leads to 133 possible transitions instead of 49, still not enough to account for the observed difference. We conjecture that the small hybridization between the europium (gadolinium)  $4f$  orbitals and the boron  $sp$  [Refs. 4 and 37] (gadolinium  $5p$  Ref. [38]) orbitals, suggested but overestimated by band structure calculations, opens the necessary extra channels. We hope that our results, which confirm previously established discrepancies, will encourage more theoretical work on this long-standing problem.

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