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ELECTRON CONCENTRATION DEPENDENCE OF TRANSPORT AND MAGNETIC PROPERTIES IN NARROW GAP SEMICONDUCTOR EuB_6

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Transport and magnetic measurements have been made on $Eu_{1-x}La_xB_6$ system in detail. Contrary to the previous report, paramagnetic Curie and ordering temperatures along with the temperature, at which resistivity shows a peak, decrease drastically with increasing the carrier number.

EuB_6 is a narrow gap semiconductor in paramagnetic state, although it behaves usually as a degenerate semiconductor due to defects and impurities. The Curie temperature T_c has been defined to be around 13 ± 1 K from magnetic and Mössbauer measurements [1-3]. Due to the narrow gap, magnetic and electronic properties show anomalous behavior. These properties have been explained in our recent paper on the stand point of the unusual character of the Eu^{2+} vacancy [1]. Recently, the pressure dependences of the transport and magnetic properties of EuB_6 were reported [4,5]. Main features are that, under pressure, the Curie temperature increases and the electrical resistivity ρ decreases with increasing the carrier number n. These features are contrary to the experimental results of $EuB_{6-x}C_x$ in which T_c and the paramagnetic Curie temperature θ_p decrease continuously with increasing the carrier number per rare earth ion, which is nearly equal to x. In $Eu_{1-x}La_xB_6$, too, the carrier number n increases nearly proportionaly to x, $n \sim x$. However, θ_p was reported to be not decreasing monotonically as a function of x but has a peak for $x \sim 0.05$ [6]. Our preliminary experiment on this system [7] shows, however, that the behavior is similar to $EuB_{6-x}C_x$ [8]. To check these contradictory results, we report our more detailed experimental results of $Eu_{1-x}La_xB_6$ system.

At first, we prepared powders of $Eu_{1-x}La_xB_6$ by borothermal reduction. For the measurements of magnetic properties, we used polycrystals prepared from the powders by melting in an arc furnace and slow cooling. For the measurements of transport properties, it is important to use single crystals and the single crystals were prepared by the Al-flux method. The typical dimensions of the samples for which transport data are presented are $1.5 \times 0.15 \times 0.05$ mm^3. A chemical analysis of the final products has not been performed, since defects and impurities may also generate free carriers. So we relate the measured value of n instead of x with magnetic and transport properties. In the arc-melt samples, nominal concentration of La content and the observed value of n deduced from Hall effect with single-band model is nearly equal; 1(0.88), 2(2.6), 4(3.9), 5(6.1) and 10%(12.2%) for samples #8, 9, 10, 11 and 12, respectively. This fact suggests that each La atom contributes in fact one conduction electron. In the Al-flux method, considerable amounts of La are dissolved into the Al-flux and single crystals with n up to 0.027 per rare earth ion were obtained.

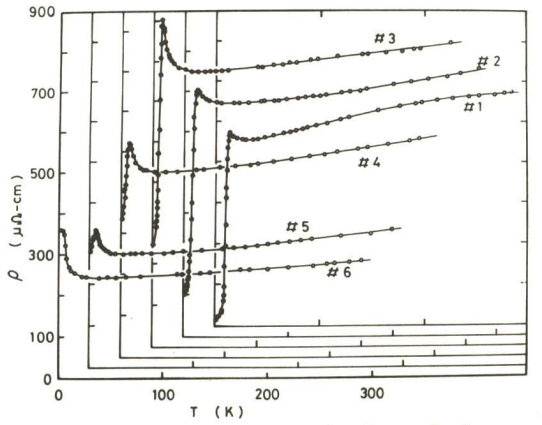

Figure 1 Temperature variation of the zero-field resistivity of samples #1, 2, 3, 4, 5 and 6

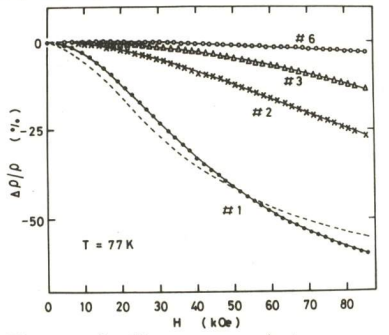

Figure 2 Magnetoresistance of samples #1, 2, 3 and 6 at 77 K: $\Delta R_o/R_o$ vs H cauve of #1 at 77 K is also shown by dashed line

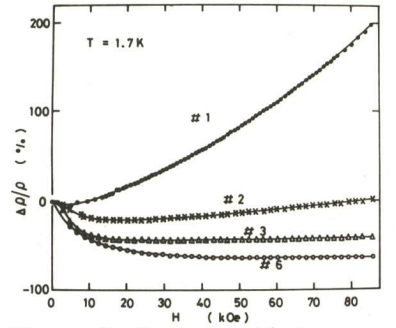

Figure 3 Magnetoresistance of samples #1, 2, 3 and 6 at 1.7 K

Measurements of dc resistivity were carried out from room temperature to 1.7 K under magnetic fields up to 85 kOe. The temperature variation of ρ, the current being in the [100] direction, is shown in Fig.1. The sample #1 is not La-doped intentionally. A peak in the zero-field resistivity was observed in each of #1, 2, 3, 4 and 5. Carrier number at room temperature deduced from the Hall effect is 0.0032, 0.0056, 0.0073, 0.013, 0.020 and 0.027 per Eu ion for #1, 2, 3, 4, 5 and 6, respectively. Therefore T_p, the temperature at which ρ shows a peak, decreases with increasing n. Furthermore, the residual resistivity at low temperatures increases with increasing n. Another prominent feature of the resistivity data is of its external magnetic field dependence (Figs.2 and 3). In #1, usual positive magnetoresistance was observed at temperature far below T_p. As temperature increases, the magnetoresistance changes its sign quickly far below T_p and the magnitude of the negative magnetoresistance is large even at 77 K. In other samples ρ decreases rapidly with increasing the external magnetic field H at low fields and becomes nearly constant at higher fields at 1.7 K. The magnetic field, at which ρ becomes constant, is higher for the samples with higher electron concentration. To investigate the origin of the magnetoresistance, we measure the Hall effect. In Figs.4-6, we show the Hall voltage vs H curves for #1, 3 and 6. In recent paper we have already shown that anomalous Hall effect is negligibly small in EuB_6 [1]. Then the Hall voltage is expressed as $V_H = R_o(H-NM+4\pi M)I/t$, where I is the electric current and t is the thickness of the sample. At ferromagnetic state, the conduction bands overlap with the valence bands [1]. However, the effective mass of the valence bands is one order of magnitude larger than that of the conduction bands [9]. Then, in interpreting our Hall effect, we neglect the current due to the valence bands and $n = 1/R_o e$ is used over the entire range of temperature. In Fig.2, we plotted $\Delta R_o/R_o$ vs H curve for #1 by the dashed line which is calculated from corresponding Hall effect in Fig.4. It is apparent that magnetoresistance is due to change in n and the contribution of the mobility is small. This may originate from the dependence of the energy gap on the magnetization. At 85 kOe, the magnetization per Eu ion is about 2 μ_B. Then the shift of conduction bands of up spin due to the d-f

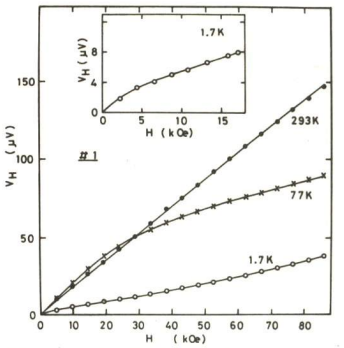

Figure 4 Hall voltage in sample #1 as a function of external magnetic field at 1.7, 77 and 293 K

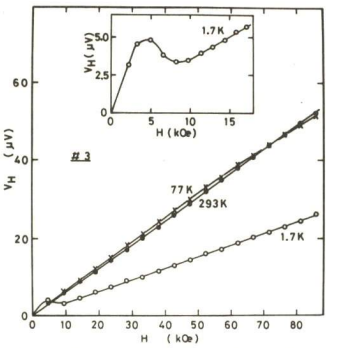

Figure 5 V_H vs H curves of #3. The insert shows more clearly the curve at 1.7 K and at low fields

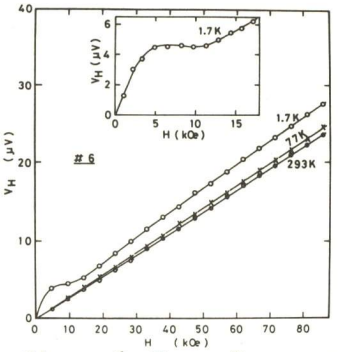

Figure 6 V_H vs H curves of #6

interaction is $I_c\langle S_f\rangle$ = 660 K and up spin valence bands shift to the opposite direction, $I_v\langle S_f\rangle$ = 330 K, due to the p-f mixing effect [1]. On the other hand, the energy gap between the valence bands and conduction bands in the paramagnetic state was evaluated to be about 200 K from the temperature dependence of the resistivity at higher temperature [1]. Therefore the bottom of the conduction bands can overlap easily with the valence bands, resulting in increase in n. At 1.7 K, largest negative magnetoresistance is observed in #6; $\Delta\rho/\rho$ is -63% at high fields (Fig.3). Corresponding Hall effect is shown in Fig.6. At high fields, n is 0.026 per Eu ion. At the lowest field, n is calculated to be 0.0085 per Eu ion. Here demagnetization corrections were performed by using the magnetization data of #9 which has nearly same value of n as #6 at 293 K. Then $\Delta R_o/R_o$ of #6 at high fields and at 1.7 K is -67%. Therefore we can conclude that the negative magnetoresistance below the magnetic ordering temperature is also due to change in n.

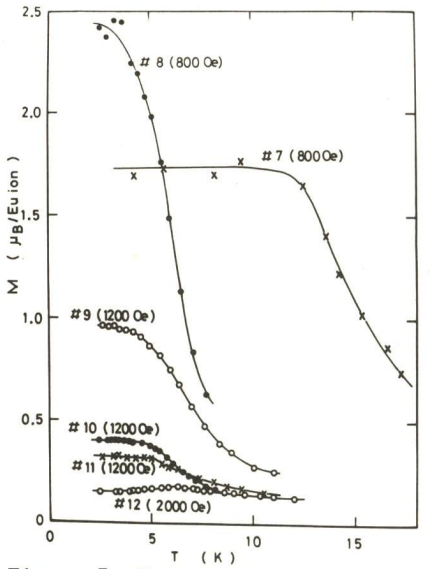

Figure 7 Temperature dependence of the magnetizations of samples #7, 8, 9, 10, 11 and 12

To know n dependence of the magnetic ordering temperature T_o, we measured temperature dependence of magnetization at low fields for #7, 8, 9, 10, 11 and 12 and plotted the results in Fig.7. The sample #7 is not La-doped intentionaly. As n increases, T_o decreases rapidly and then increases slowly above n = 0.02. There is a peak in the magnetization vs temperature curve for #12. A negative value of the paramagnetic Curie temperature Θ_p, -5 K, suggests that #12 is the antiferromagnetic. For samples with intermediate value of n, the susceptibility is field dependent at low fields and the magnetization does not saturate easily; 5.6 and 3.3 μ_B per Eu ion for #8 and 9 at 1.7 K and at 10 kOe, respectively. These results along with magnetoresistance data (Fig.3) suggest that increase of the ferromagnetic moment under the magnetic field may accompany increase in n and magnetic structure of the samples with inter-

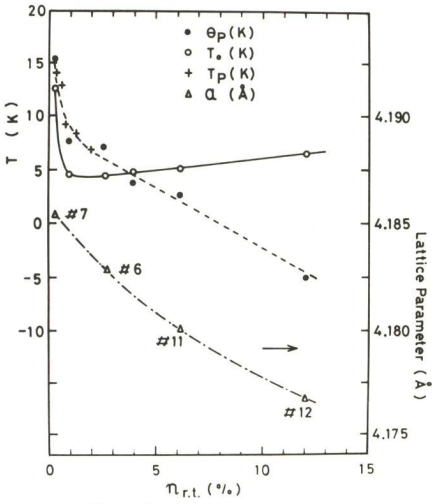

Figure 8 Electron concentration dependence of Θ_p, T_o, T_p and a

mediate value of n is complex such as cone spiral. In Fig.8, we summarize n dependence of T_o, Θ_p, T_p and the lattice parameter a. There is a good coincidence between T_p and Θ_p but T_o is a little bit smaller for lower values of n. These results are essentially same as those obtained in $EuB_{6-x}C_x$ [8] but inconsistent with the results measured by Mercurio et al. on $Eu_{1-x}La_xB_6$ [6].

The fact that all of Θ_p, T_p and T_o decrease monotonically with increasing n, in particular sharp decreasing for low region of $n < 0.01$, is unusual and is not explained so far. The following reasons may be considered. (i) Intervalley d-f exchange scattering may be important, which causes antiferromagnetic ordering. (ii) The third hole trapped to each Eu defect is filled rapidly with increasing n, which will leave two trapped holes with antiparallel spins and thus destroy the giant spin cluster around each Eu defect. (iii) As n increases, the Fermi energy E_F increases relative to the top of the valence band, which causes quick decrease and disapperence of the second Curie temperature T_{c2}, at which the magnetic induced metal-insulator transition occurs and the strong ferromagnetism begins to occur [1]. These effects seem to cause also decrease in the first Curie temperature T_{c1}. More detailed investigation is necessary to clarify real mechanism. It is clear that the pressure effect is different from the alloying effect to increase n. The mechanisms (ii) and (iii) mentioned above do not exist in the pressure effect. Under pressure the gap between the conduction and the valence bands decreases, resulting in decrease of the Fermi energy measured from top of the valence band. Calculated results on the pressure effect will be published in a separate paper [10].

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