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IV. TRANSPORT.

ELECTRONIC STRUCTURE OF EuB_6 , TRANSPORT AND MAGNETIC PROPERTIES

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Résumé.— On montre que dans les composés non magnétiques R^{++}B_6 , le défaut le plus courant, la lacune R^{++} , peut piéger un troisième trou en créant un électron de conduction comparateur, ceci à cause du caractère de semiconducteur à bande interdite étroite. Cet électron est faiblement piégé et donc donne lieu facilement à une conduction de type n. Différentes propriétés de transport sont expliquées par ce modèle. Dans EuB_6 magnétique le défaut précédent forme un amas à moment géant. De plus, à cause de l'effet d'anti-liaison avec les niveaux 4f, les bandes de valence de spin parallèle sont faussées à l'intérieur des bandes de conduction dans l'état ferromagnétique, créant plusieurs électrons de conduction. Différentes propriétés anormales magnétiques et de transport sont expliquées dans ce modèle.

Abstract.— In non-magnetic R^{++}B_6 , it is shown that the most common defect R^{++} vacancy can trap third hole creating a compensating conduction electron due to the narrow gap semiconductor character. The latter is trapped loosely and thus easily causes n-type character. Various transport properties are explained on this model. In magnetic EuB_6 , the above defect center makes a giant moment cluster. Furthermore, due to the antibonding effect with the 4f levels, the valence bands of the parallel spin are pushed up into the conduction bands in ferromagnetic state creating many conduction electrons. Various anomalous magnetic and magneto transport properties are explained on this model.

1. **Introduction.**— Rare earth hexaborides, RB_6 , have the CsCl type structure in which an octahedral B_6 molecule replace a Cl atom. The bonding bands of the boron network require two extra electrons per cell and thus the divalent rare earth hexaborides are insulators. Both experiment and band calculation show that the gap between the valence and the conduction bands is very narrow, a few tenths of eV [1,2,3]. The most probable defect of this structure is the R^{++} vacancy [4] which should, in usual sense, causes the p-type character. On the contrary, however, nearly all materials measured so far are n-type. At first, we discuss this peculiar problem as the character of the impurity state in narrow band semiconductors because the characteristic properties of this type of impurity state have also very important magnetic effects in EuB_6 .

EuB_6 had been reported to be a ferromagnet with a Curie temperature T_c of about 10K [5]. The first single crystal made by us was, however, complicated anti-ferromagnetic type showing various kinds of anomalous properties [6]. Careful sample

preparation and measurements on various physical properties indicate again that the purest EuB_6 is ferromagnetic and the single crystal we made before includes a few percent of carbon [7,8]. However, detailed investigation on pure EuB_6 raised new puzzles that purest EuB_6 is also very anomalous in its magnetic and electronic properties [9,10]. In §3, we treat this problem on the stand point that the valence bands couple strongly with the 4f states causing very unusual behavior and, even in purest sample, the unusual impurity state mentioned before plays an important role. In §4, anomalous properties of carbon doped EuB_6 are treated on the same stand point.

2. **Electronic Structure of YbB_6 .**— As a typical non-magnetic divalent hexaboride, YbB_6 is considered in detail. In figure 1, electrical resistivities of pure and carbon doped YbB_6 are shown up to 1,000K of temperature. It is apparent that in pure YbB_6 the effect of the valence bands becomes clear above room temperature, while in carbon doped sample no effect is observed up to 800K because of a large Fermi energy.

Fig. 1: Experimental values of the electrical resistivities are shown by $\circ$ for YbB_6 and $\text{YbB}_{5.93}\text{C}_{0.03}$, $\blacktriangle$ for EuB_6 #1 and $\bullet$ for $\text{EuB}_{5.95}\text{C}_{0.05}$ /24/. Calculated fitting curves are shown by solid lines. See Table I for the fitting parameters. For carbon doped samples, the calculated values for $B = 0$ are shown by broken lines.

From these facts, the top of the valence bands is expected to be about 1,000 ~ 2,000 K below the bottom of the conduction bands. From the Hall constant, the number of the conduction electron n_c at 300K is 17% larger than that at 77K in YbB_6 but is nearly constant in carbon doped YbB_6 as shown in table I.

Table Ia : Transport properties of carbon doped samples $\text{RB}_{6-x}\text{C}_x$. The numbers of conduction electrons at 77K and 300K are fitted. Various fitting parameters shown in the text, A , E_0 , a , E_{i1} and E_{i2} are tabulated. E_{F0} , the Fermi energy at $T=0$, $\rho_{4.2}$, resistivity at 4.2K, and the number of the Eu defect n_i are also shown.

	$\rho_{4.2}$ ($\mu\Omega\text{cm}$)	n_c^{77} (n/Formula unit)	n_c^{300} (n/Formula unit)	E_{F0} (K)	n_i (n/Formula unit)	A ($10^{-8}\text{Kcm}^3/\text{sec}$)	E_0 (K)	E_{i1} (K)	E_{i2} (K)	a ($10^{-8}\text{Kcm}^3/\text{sec}$)
$\text{YbB}_{5.97}\text{C}_{0.03}$	31	0.021	0.021	3600	0.01	22.49	0	5100	2100	8.10
$\text{EuB}_{5.95}\text{C}_{0.05}$	170	0.023	0.023	3757	0.03	17.98	500	5257	2257	27.59
$\text{EuB}_{5.97}\text{C}_{0.03}$		0.03	0.03							

Note that all of them are n-type. It is now well established both from experiments and from band calculations that both the bottoms of the conduction bands and the tops of the valence bands are at the three X points. The effective mass of the conduction bands at the Fermi energy of LaB_6 is about 0.5m, becoming smaller with decreasing energy, and is expected to be 0.2 ~ 0.3m near at the bottom /11,12,13/. On the other hand, the effective mass of the valence band is expected to be much larger at the top but there are no definite experimental evidences.

Now let us consider at first the mechanism for the n-type character in most samples. The most probable defect is considered to be R^{++} vacancy /4/ because the borons make a stable bonding network. Then, as was shown before by us /14/, even the third extra hole can be localized mostly on the nearest neighbour B_6 molecules with a binding energy of about a few tenths of eV and then this impurity hole state is pushed up into the conduction bands and thus creates one compensating conduction electron. This electron is trapped loosely to the impurity complex with one positive effective charge but is very easily delocalized showing n-type conduction because of a small effective mass and the screening

Table Ib : Transport properties of pure RB_6 . n_c^{77} and n_c^{300} are fitted. Fitting parameters, a , A , E_0 , E_i and α are tabulated.

	$\rho_{4.2}$ ($\mu\Omega\text{cm}$)	ρ_{30}	n_c^{77} (n/Formula unit)	n_c^{300} (n/Formula unit)	E_{FO} (K)	n_i (n/Formula unit)	A ($10^{-8}\text{Kcm}^3/\text{sec}$)	E_0 (K)	E_i (K)	α	a ($10^{-8}\text{Kcm}^3/\text{sec}$)
YbB_6	280		0.00056	0.00064	321	0.0008	10.12	-1500	595	0.7	6.23
EuB_6 #1	12	350	0.0015	0.0022	609	0.0017	24.73	-180	1217	0.9	14.43
#2	35	800	0.0055	0.0067	1447	0.0079	24.73	900	1721	0.7	58.69
#3	10	350	0.004(?)		1170	0.0015	24.73	0	1171	0.5	27.65

effect. It is expected that the holes are localized even for a few percent of the vacancies, while the electrons are delocalized even for 0.01% of vacancies which are expected to be even in the purest sample. With increasing number of R^{++} vacancies, the Fermi energy of the delocalized conduction electrons increases and the third hole band will be filled partly. This seems to be the situation of the so called pure YbB_6 . The situation is illustrated in figure 2.

Fig. 2 : Schematic picture for a R^{++} defect center.

When carbons are doped, each of which substitutes a boron and thus supplies one conduction electron, the third holes around R^{++} vacancies are filled easily, and furthermore the second and finally the first holes are also filled. The situation of a few percent carbon doped sample seems to be in such a state and, for more than several percent of doped carbon, all the impurity holes seem to be filled causing normal

magnetic and transport properties. Note that the hole impurity states are not the real localized states but the virtual bound state mixed with the conduction bands, in the similar sense as the usual d virtual state in the transition metal impurities. Note, however, that, because of the large correlation effect compared with the mixing energy, the nearly complete orbital splitting is expected in contrast with the 3d case. The width of the virtual bound state is thought to be the same order of the energy of the conduction band at the bound state, that is, 1,000 ~ 2,000 K. The width due to the potential fluctuation is also expected to be the similar order.

Next, the resistivity of carbon doped sample is considered. When the scattering matrix is constant, the phonon scattering resistivity ρ_p is inversely proportional to the Fermi energy E_F . Actually, the relation is applicable in comparison with LaB_6 , that is, $E_F = 0.26$ and 2eV for the effective mass ratio $m_c/m = 0.3$ and 0.5, and $\rho_p = 70$ and 9 $\mu\Omega\text{cm}$ for $\text{YbB}_{5.97}\text{C}_{0.03}$ and LaB_6 , respectively. An unusual property in $\text{YbB}_{5.97}\text{C}_{0.03}$ is the sharper than T linear increase of the resistivity in high temperature region. This is attributed to the situation that the Fermi level is in between the second and the first bound states. Note that as the carbon concentration increases, the Yb vacancies also increase by compensation. In the present sample,

about 1% of Yb vacancies are expected to be formed absorbing 1% of conduction electrons supplied by carbon leaving $n_c = 0.02/\text{Yb}$ as shown in table I. As an example, the calculated results based on the model shown in figure 3 are compared with experiment in figure 1. The electrical resistivity ρ is calculated by the following form

$$\rho^{-1} = e^2 L_{00} \quad (1)$$

$$L_{nm} = \frac{2v(2m_c)^{1/2}}{3\pi^2 \hbar^3} \int_0^\infty E^{3/2} (E-\mu)^{n+m} \tau(E) f(E) \times (1-f(E)) \frac{dE}{kT} \quad (2)$$

in which we assumed that only the conduction electrons carry the currents. Here, $v=3$ is the number of the valleys in the conduction bands, μ the Fermi energy, $f(E)$ the Fermi distribution function. The effective mass near the bottom of the conduction band is taken to be $m_c = 0.25m$. The life time $\tau(E)$ is given by

$$\tau(E)^{-1} = a [N_c(E) + B(N_i(E) + N_v(E))] + A\rho_{op}(\hbar\omega/T) [N_c(E) + B(N_i(E \pm \hbar\omega) + N_v(E \pm \hbar\omega))] \quad (3)$$

in which the first term means the impurity scattering and the second term the phonon scattering with

$$\rho_{op}(x) = x n(x) (1 + n(x)) \quad (4)$$

in which $n(x)$ is the Bose distribution function. Several comments should be done concerning the above form. (i) The density of states for the conduction band is given by the usual effective mass form of the three valleys. (ii) Concerning the valence bands, we have not enough information. A very interesting information comes from KB_6 , which should be metallic with a hole per K atom but is an insulator with a small gap experimentally /15/. A possible interpretation may be as follows. The characteristic property of the top of the valence band is the non-bonding character in $[100]$ directions /16/. Then, the Fermi surface of KB_6 is expected to be formed by three nearly parallel pipes with a rather rectangular cross section due to the non-linear disper-

sion in the perpendicular directions. Then we can expect formation of multiple charge density waves probably with six $[110]$ directions of the wave vectors, or may be three $[100]$ directions, which create a small gap. In this respect, the valence band is described rather well by the two dimensional dispersion. At the top of the valence band with a small number of the hole, however, three dimensional dispersion seems to be applicable, and we use the effective mass $m_h = 2m$ in the following calculation, which is larger than that of the band calculation /3/ but agrees better with experimental results. (iii) The shape of the virtual bound state is assumed to be as follows,

$$N_i(E) = n_i \frac{3}{4} \left(\frac{2}{\Delta}\right)^3 \left[\left(\frac{\Delta}{2}\right)^2 - (E-E_i)^2\right] \quad (5)$$

which gives the number of the defect n_i by integration with respect to E . The binding energy $E_i - E_0$, in which E_0 means the top of the valence bands, is expected to decrease with increasing number of n_c . (iv) Inelastic character should be included in the phonon scattering to the valence bands. This effect is, however, not important in the scattering to the conduction bands and then neglected. (v) The scattering to the virtual bound states should be treated in principle on the standpoint of the resonance scattering. In the present calculations, however, we used the more conventional model and treated the valence band and the virtual bound state similarly. More careful check of this point will be done in the forthcoming paper. (vi) In usual ionic crystal, an electron near the bottom of the band is scattered mostly by the longitudinal optical phonons because the coupling constant is inversely proportional to the scattering vector q . With a finite number of conduction electrons, the coupling constant as well as the optical phonon frequencies is screened very quickly. This screening process depends sensitively on temperature because the numbers of conduction electrons and, more importantly, valence electrons change with temperature,

which causes sensitive effect on the transport.

Fig. 3 : Density of states $N(E)$ is shown as a function of energy E for a; paramagnetic region and b; ferromagnetic region for up and down spins.

We found, however, that various transport phenomena are not fitted consistently with the intravalley optical phonon scattering but are fitted well by the inter-valley scattering. In this sense, the latter model was used with the typical phonon $\hbar\omega = 300\text{K}$ /17,18,19/. (vii) The parameter a is given so as to fit the residual resistivity. B is chosen to be a constant 0.5. Then, actual adjustable parameters are A , E_0 and α , the fraction of unoccupied part of the bound state. These parameters are given in table I. In carbon doped samples, the energy difference between the second and the first bound states is chosen tentatively to be 3,000K.

In the case of YbB_6 , sharp decrease of the resistivity is observed above room temperature, which is due to the sharp increase of the conduction electron creating holes in the valence band, where E_0 is chosen to be -1500K. Note that in the carbon doped sample the sharp increase of n_c occurs above 1,000K. The value of A is small in YbB_6 compared to other samples. The reason is not clear. α is evaluated to

be near unity, 0.8 to 0.9, which suppresses n_c at lower temperature and thus important to fit n_c^{300} .

3. EuB_6 .— At first, let us consider the resistivity of a carbon doped sample $\text{EuB}_{6-x}\text{C}_x$, $x=0.05$, in the paramagnetic region. Because the number of conduction electrons is similar to that of carbon doped YbB_6 , the behavior of ρ is also similar. One remarkable feature is the stronger concave character, which is consistent with the larger number of the defect expected from the larger number of doped carbon. See the broken curves in figure 1, which neglect the impurity states. Another character is the larger residual resistivity, more than three times as large as that of $\text{YbB}_{5.97}\text{C}_{0.03}$, which is also consistent with the fact that the number of the defect is also expected to be about three times. Remaining fraction should be due to the d-f exchange scattering, which is estimated from another carbon doped sample, $\text{EuB}_{5.97}\text{C}_{0.03}$, to be about $25\ \mu\Omega\text{cm}$ as shown in figure 4.

Fig. 4 : Resistivities of $\text{EuB}_{5.97}\text{C}_{0.03}$ under various magnetic fields shown in the figure. ρ_{mag} is estimated from the dotted line and the value for 85K0e.

From this value, we can estimate the square average value of the d-f exchange

constant $I_{df}^{eff} = \langle I_{df}^2 \rangle^{1/2}$ to be 0.035 eV for $m_c = 0.25m$. While, in GdB_6 , I_{df}^{eff} is estimated to be 0.05 eV for $\rho_{mag} = 15 \mu\Omega\text{cm}$ /20/, which is consistent with the fact that the 5d atomic character is about 50% at the bottom of the conduction band, increasing to 70% in the middle of the band /3,13/.

In EuB_6 , the resistivity depends sensitively on sample. In figure 5, we show three examples, #1, 2 and 3. #1 is considered to be purest, #2 includes about four times of defects and #3, reported by Fisk et al. /10/, may have the same amount of the Eu-vacancies as that of #1 and a larger amount of some n-type impurities, probably Al /21/.

Fig. 5 : Resistivities of three typical examples of EuB_6 . Experimental values are shown by $\bullet$, $\circ$ and $\square$ for #1, #2 and #3 samples, respectively. Calculated total resistivities are shown by solid lines and the disordered scattering term by broken curves. The values at 4.2K are shown by arrows.

Let us consider the paramagnetic region. The behavior of #1 is similar to YbB_6 but the relative change of n_c at room temperature is larger in #1 even if n_c^{77} is larger. This means that the valence band is closer to, or may overlap with, the conduction band. One possible mechanism is the antibonding

effect with the 4f states, which is expected to be about 1 eV below the bottom of the conduction band /22/. Both the Hall effect and the resistivity are fitted well by using the parameter listed in table I. Note a nearly unity value of α . Weaker decrease of resistivity above room temperature compared with YbB_6 seen in figure 1 is simply due to a larger initial value of n_c . Note that, among the observed residual resistivity, the d-f exchange resistivity is evaluated to be about $180 \mu\Omega\text{cm}$, attributing remaining $170 \mu\Omega\text{cm}$ to the defect scattering resistivity. Note also that the elastic scattering resistivity also shows fairly large temperature dependence as shown by broken line in figure 5 due to the temperature dependence of μ and n_c . In #2 sample, the residual resistivity is large because, compared with n_c , the number of defect n_i is large and furthermore each impurity scattering is larger because of a small value of α , indicating the near resonance scattering. Fitting parameters are shown in table 1. In #3 sample, n_i is expected to be similar to #1 and n_c is supplied mostly by shallow n-type donors. In this case, too, a smaller value of α keeps the residual resistivity in the same level as #1 and lower the temperature dependence of the total resistivity. Note that the binding energy of the virtual bound state decreases with increasing number of conduction electrons, and, as the Eu-vacancies increase, the energy of the conduction band is lowered relatively to that of the valence band, which keeps the third bound state near the Fermi level causing relatively small decrease in α . For the case of shallow donors, lowering of the conduction band seems to be weak.

With decreasing temperature, a giant moment is formed mostly by the six nearest neighbour Eu sites of each Eu-vacancy because a large indirect ferromagnetic exchange interaction exists through the vacant valence holes (bonding effect). The energy shift of the valence band (4f level)

due to the antibonding (bonding) effect is evaluated by the band calculation to be about 2,000K for the full polarization of the 4f spin S , which is consistent with a rough estimation of the atomic picture. This gives $I_V \sim 300K$ in the form of $I_V S \alpha_V$, in which α_V is the Pauli operator of the valence electron. Therefore, the giant moment around a defect is estimated to be formed at about 50K. Once the giant moment is formed, the energy of the bound hole is pushed up causing increase in the Fermi energy and thus n_C . In the ferromagnetic region, the valence band of up spin shifts up about 1,000K and down spin down 1,000K. On the other hand, the conduction bands move oppositely. The intraband d-f exchange constant I_C is evaluated to be about 600K both from I_{eff} estimated before and assuming that the intervalley interaction is small and the 50% of the 5d character at the bottom of the conduction band and the atomic d-f exchange $I_{df}^0 = 0.1eV$. Then the shifts of the conduction bands are about $\pm 2000K$ for $\pm$ spins. The situation is illustrated in figure 3b. A remarkable result is large increase of n_C . Actually, in various EuB_6 , n_C obtained from the Hall constant at 4.2K increases five $\pm$ one times compared with that at 77K. The following combinations of I_C and I_V are consistent with the above result; $(I_C, I_V) = (465, 465)$ and $(620, 310)$ K. As was estimated before, the real combination seems to be closer to the latter. Decrease of the resistivity is larger than n_C , in #1, for example, 1/35 for the total residual resistivity and 1/17 for the defect scattering resistivity. This means that the defect scattering constant decreases rapidly with increasing number of n_C . For example, in #2, the residual resistivity ratio is 1/23 and in the ferromagnetic region $n_C = 0.028/Eu$ and $\rho_0 = 35 \mu\Omega cm$. Compared with $YbB_{5.97}Co_{0.03}$, n_C is a little bit larger and the defect concentration is a little bit smaller but ρ_0 is nearly equal. This difference is explained consistently by the coexistence of the

valence band holes in #2.

The magnetic properties may be evaluated in the following ways. Here, only the free part, which means outside of the giant moment, is treated and the effect of the giant moment is treated by the effective field H or the effective moment M_0 . (More detailed treatment including the giant moment self-consistently will be given in a separate paper.)

$$E_{C\sigma} = E_C^0 - I_C \sigma (M_f + \alpha M_0) - \mu H \sigma \quad (6)$$

$$E_{V\sigma} = E_V^0 + I_V \sigma (M_f + \beta M_0) - \mu H \sigma \quad (7)$$

$$F = F_e - g \mu H M_f - J M_f^2 - kT \phi(M_f) \quad (8)$$

in which $M_f = \langle S_f \rangle$, F_e is the Free energy of the conduction and the valence electrons per Eu atom and $\phi(M)$ is the entropy of each 4f spin. M_f is determined by minimizing $F(M_f)$. In figures 6 and 7, temperature dependence of M and C , specific heat, is shown. In the case I, $I_C = I_V$, the transition occurs at $T_{C2} = 7K$ in the first order promoted by the valence band. In the case II, $I_C = 2I_V$, the usual second order transition occurs at about $T_{C1} = 8K$ due to the conduction electrons. When the direct ferromagnetic coupling between 4f spins is introduced, which is expected to be the same mechanism as that in Eu-chalcogenides treated by us /23/ and the value $J = 0.4K$ is also reasonable, T_{C2} remains nearly constant but T_{C1} is enhanced and increases to 13K in agreement with experiment. Below T_{C1} , however, saturation of the polarization of the conduction electron spin occurs easily and thus M_f is kept small and the specific heat is also small. When the effect of the giant moment is included, the sharp transitions are smeared out and the agreement with experiment becomes better. Note that the result of our specific heat measurement agrees very well with that of Fisk et al./10/ below 12K, but above 12K our value is about a half of theirs. This may be due to the difference of the defect number. Actually there is a long tail due to the giant moment formation (fig. 7).

Fig. 6 : Magnetization M of #4 sample are plotted as functions of temperature T . $\circ$ is obtained from the extrapolation of the Arrott plot at $H_{int}/M=2\text{kOe}/\mu_B/\text{Eu}$ and $\bullet$ is the value at $H_{int}/M=0.5\text{kOe}/\mu_B/\text{Eu}$. Solid curve is obtained by calculation for $I_c=620\text{K}$, $I_v=310\text{K}$, $J=0.4\text{K}$ and $M_0=H=0$. Broken curve is obtained by including $\mu_B H=0.25\text{K}$.

Fig. 7 : Magnetic specific heat C , obtained by subtracting that of LaB_6 , of #5 EuB_6 , for comparison, that of $\text{EuB}_{5.97}\text{Co}_{0.03}$ are shown by $\circ$ and $\bullet$, respectively. Calculated values are shown by solid and broken lines. The parameters used are the same as those in figure 6. The dotted curve is the expected theoretical curve by taking into account a local fluctuation of the giant moment.

Note also that our molecular field model calculation fits the experimental T linear dependence below T_{c2} very well. From the Arrott plot, we found that T_{c1} is nearly constant, $13\sim 14\text{K}$, in various samples which show different transport behaviors. This means that T_{c1} is intrinsic and the main effect of the giant moment around the defect

is to smear the sharp transitions at T_{c1} and T_{c2} .

Finally, the transient temperature region near above T_{c1} is considered. There are two main effects. One is the giant moment formation as was described before. Another is the shift of the conduction and valence bands due to the short range order of $4f$ spins. The situation is illustrated schematically in figure 8. There are various anomalies both in transport and magnetic behaviors. For example, a peak is observed in resistivity several degrees above T_{c1} .

Note that our polycrystalline samples give correct intrinsic informations on magnetic, electronic and transport properties such as Hall effect and thermoelectric power except the absolute value of resistivity. Various properties of #4 are very similar to these of #1 except a large peak of resistivity. T_c is evaluated to be 13.9K from the detailed Arrot plot. As shown in figure 9, the peak disappears for only 2.7kOe of the applied field. Note that $n_c = 0.0026/\text{Eu}$ at 300K, 0.0016/Eu at 77K and 0.0081/Eu at 4.2K. Three possible mechanisms, resonance scattering by the giant moment, usual ferromagnetic critical scattering and shift of the top of valence band to the Fermi level by the short range ordering, are considered but it is difficult now to select one from others as the most important. A sharp structure is observed also in the thermoelectric power of #4 as shown in figure 10.

Fig. 10 : Thermoelectric power ϕ of EuB_6 #4 is plotted as a function of T . For comparison, ϕ of $\text{EuB}_{5.97}\text{C}_{0.03}$ is also shown.

For the thermoelectric power, more detailed informations on the energy dependence of the scattering matrixes are involved and we have not yet done the detailed quantitative fitting. But the sharp decrease at

about 30K seems to suggest the effect of giant moment formation. The giant moment effect is also seen in the induced moment above T_{c1} as shown in figure 6.

4. Carbon doped EuB_6 .— Because there remains no space any more, this topic is sketched very briefly. For samples of $n_c \sim 0.02 \sim 0.03/\text{Eu}$ in the paramagnetic region, the top of the valence band can not reach the Fermi level even in the perfect 4f spin alignment and thus n_c is nearly constant in the whole temperature region. Anomalous behavior is, thus, mostly due to the giant moment through the first hole trapped by the Eu defect. Furthermore, as k_F increases, the intervalley exchange becomes important and thus the complicated spin ordering is rather realized. The detail will be given in a separate paper.

5 Conclusion.— Due to the narrow gap character, a R^{++} vacancy can trap the third hole on the nearest neighbour B_6 molecules, which creates a compensating loosely trapped conduction electron. Various anomalous transport properties are explained by this model. At low temperature, the above defect center forms a giant moment in EuB_6 and furthermore, the valence bands with the parallel spin are shifted up through the antibonding effect with the 4f spins, creating a lot of conduction electrons and causing the first order transition to the strong ferromagnetism at T_{c2} . The second order transition at a higher temperature T_{c1} is due to the conduction bands and the direct 4f exchange interaction, which cause a weak ferromagnetism because the conduction electron spins saturate very quickly. The giant moments smear the sharp transitions at T_{c1} and T_{c2} . Anomalous magnetic and transport properties in EuB_6 are explained on the above model.

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