

## Review

### Resistance minimum and heavy fermions

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**Abstract:** The phenomenon of the resistance minimum in dilute magnetic alloys is explained in terms of the s-d interaction which takes account of scattering of the conduction electron off the magnetic impurities in metals. Some of the intermetallic compounds which involve rare earth elements or uranium show a very large electronic specific heat and remain non-magnetic even though they show a Curie-like susceptibility at higher temperatures. These phenomena are also explained based on the s-d interaction model.

**Key words:** Resistance minimum; magnetic impurity; heavy fermion; Kondo effect.

**1. Introduction.** The electrical resistance of a metal usually decreases as the temperature is decreased. This is because the atomic vibration which causes the electrical resistance calms down and the electrons tend to move freely in the metal as the temperature is decreased (Fig. 1 (a)). Another cause of the resistance is the impurity atom and the resistance arising from this cause is independent of the temperature. When these two causes coexist, the resistance looks like Fig. 1 (b). However, when a small amount of atoms like manganese or iron are put into, e.g., copper, the resistance first decreases as the temperature is decreased but then tends to increase towards low temperature like liquid helium temperature (Fig. 1 (c)). The turn-over temperature is typically 20 K and the value of the resistance increases about 10% by 4 K. In this case the impurity atom of manganese or iron possesses a spin and is called magnetic impurity, which behaves like a small magnet. This phenomenon (Fig. 1 (c)) is called the resistance minimum, and turned out to occur inevitably when noble metals and di-valent metals involve small amount (less than 1 atomic per cent) of magnetic impurities.<sup>1)</sup> This phenomenon interested many people and has been discussed by these people from the time of the first international conference on low temperature physics. The main concern was the cause of the

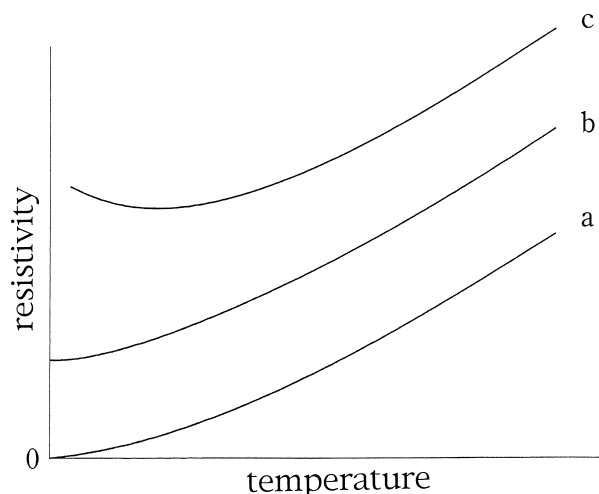


Fig. 1. Temperature dependence of the electrical resistivity of a metal. a: pure metal, b: metal involving impurities, c: metal involving magnetic impurities.

resistance minimum but the answer was not easily obtained. In this article I shall mention a theoretical explanation of it and touch upon a related subject of heavy fermion systems.

Before mentioning the main subject I shall mention the difficulties of the problem from theoretical point of view. The fact in question is that the electrical resistance arising from magnetic impurities *increases* as the temperature goes down. In general the cause of the electrical resistance, e.g. atomic vibration, calms down as the temperature decreases and

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so the resistance also decreases. Thus the inverse is hard to be realized. Furthermore, the fact that the resistance minimum occurs at low temperatures such as 20 K is a hard question to answer. This fact implies that the things which cause electrical resistivity are not settled but perform internal motion even at these low temperatures. For example in the case of iron impurity in gold the resistivity continues to increase even at temperatures as low as 0.01 K<sup>2)</sup> and one may wonder what is changing in the iron atom at such a low temperature. One more thing difficult to explain is that the resistance minimum always occurs when a metal contains small amount of magnetic impurities. Suppose that one took a special model and could overcome the difficulties mentioned above for some magnetic alloys. He then must proceed to explain anomalies of other magnetic alloys. But the special model would not be applicable to any other magnetic alloys. Thus one must use a standard and simple model, which had, however, been studied enough and turned out not to be useful to explain the resistance minimum.

I shall mention how these difficulties were overcome. Roughly speaking I took a model which is so universal as applicable to most magnetic impurities and devised the way to calculate the resistivity using the universal model. In our case the cause of the resistivity is the scattering of the free electrons in the metal off the magnetic impurity, which possesses a spin. The direction of the spin may be up or down in the case of  $S=1/2$ . In the previous calculations the spin direction was fixed to up or down but actually the direction changes from time to time due to the interaction between the spin and the metal electrons. I took account of this fact into my calculation and this was achieved by calculating the higher-order corrections to the previous calculation.<sup>3)</sup> The correction term turned out to depend on the temperature and cleared the difficulties mentioned above. Before going into this subject some preliminaries are necessary.

## 2. Free electron model of the metal.

In the case of copper metal, e.g., the copper ions have a valence +1 and are arranged regularly forming a lattice in which the electrons are traveling. One may consider that these electrons are moving as freely as molecules in a gas, so they are called free electrons. Its energy is given by  $m\mathbf{v}^2/2$ , where  $m$  is the mass of the electron and  $\mathbf{v}$  is its velocity. The total energy of the electrons is obtained by summing this

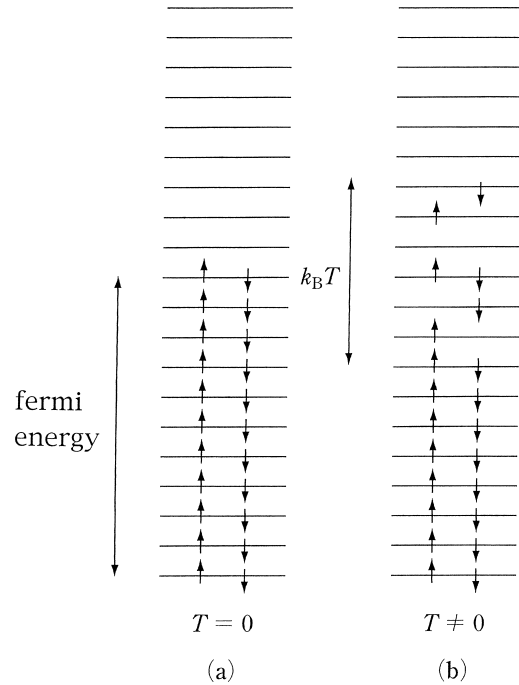


Fig. 2. Energy levels of the free electron of a metal. (a) At zero temperature each level is occupied by two electrons from the lowest level. (b) At temperature  $T$ , levels in the range  $k_B T$  around the fermi energy are either occupied by the electron or empty.

energy for all the electrons. At zero temperature the system is in the lowest energy state, where not all the electrons are in the state  $\mathbf{v} = 0$ . The value of  $\mathbf{v}$  is quantized and each quantized state is occupied by an up-spin electron and a down-spin electron. When all the electrons are distributed from the low energy states, the highest energy of the electron will be about electron volts and its velocity will be about  $10^8$  cm/sec. This highest energy is called the fermi energy (Fig. 2(a)) and is written as  $\epsilon_F$ . In the  $v_x, v_y, v_z$  space the constant energy surface is a sphere, because the energy depends only on the magnitude of  $\mathbf{v}$ . The constant energy surface corresponding to the fermi energy is called the fermi surface and the sphere enclosed by it is called the fermi sphere. All the states inside of the fermi sphere are occupied by two electrons (up and down spin) and all the states outside of it are empty.

Suppose that the system is at the temperature  $T$ . Then the electron receives an energy of the order of  $k_B T$  ( $k_B$ : the Boltzman constant) from the surroundings and jumps up to an upper level. But this is possible only for the electrons whose energy is

close to the fermi energy. For the electron far below the fermi energy the energy  $k_B T$  is too small to raise it above the fermi energy. The energy levels below the fermi energy are already occupied by other electrons and Pauli's principle prevents the electron to jump into these levels. Thus thermal excitation of the electrons takes place only in the energy range of the order of  $k_B T$  around the fermi energy (Fig. 2 (b)). Consequently the states in this energy range are either occupied by an electron or empty.

Now suppose that there are impurity atoms in the sea of the free electrons. For example there may be zinc atoms in the host metal copper. The zinc atom has a valence +2, which is larger than that of copper. Then the free electrons feel this extra charge of zinc and so its velocity  $\mathbf{v}$  is no longer a constant but makes change, namely the electron is scattered. This causes the electrical resistance. In quantum mechanics the rate of such scattering (or transition of the electron state) is a matter of concern. In quantum mechanics the state of velocity  $\mathbf{v}$  is represented by a plane wave of the wave number  $\mathbf{k} = m\mathbf{v}/\hbar$  and its wave function is expressed by  $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}$ . Here  $\hbar$  is the Planck constant  $h$  divided by  $2\pi$ . From now on we shall use  $\mathbf{k}$  instead of  $\mathbf{v}$ . When we calculate the transition rate from  $\mathbf{k}$  to  $\mathbf{k}'$ , it is necessary to find the matrix element of the transition, which is expressed by

$$V_{\mathbf{k} \rightarrow \mathbf{k}'} = \int \psi_{\mathbf{k}'}^*(\mathbf{r}) V(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) d\mathbf{r}.$$

Here  $V(\mathbf{r})$  is the potential which the electron feels. The transition rate which we denote as  $W_{\mathbf{k} \rightarrow \mathbf{k}'}$  is proportional to the absolute square of the above expression and is not zero only when  $\mathbf{k}$  and  $\mathbf{k}'$  have the same energy. We define  $\gamma_{\mathbf{k}}$  by  $\gamma_{\mathbf{k}} = \sum_{\mathbf{k}'} W_{\mathbf{k} \rightarrow \mathbf{k}'}$ , which is the probability with which the electron  $\mathbf{k}$  changes into any other state and is directly related to the electrical resistivity.

Now we must know which electron contributes to the electrical resistivity. To find the answer to this problem let us consider the case when the electric field  $\mathbf{E}$  is applied to the system. Then each electron is accelerated according to the equation of motion  $d\mathbf{v}/dt = -e\mathbf{E}/m$ , where  $-e$  is the charge of the electron. Then in the  $v_x, v_y, v_z$  space every electron in the fermi sphere will move in the direction opposite to  $\mathbf{E}$  (because of the negative sign of the electron charge). Then the number of the electrons with the velocity  $\mathbf{v}$  parallel to  $\mathbf{E}$  decreases and that with the

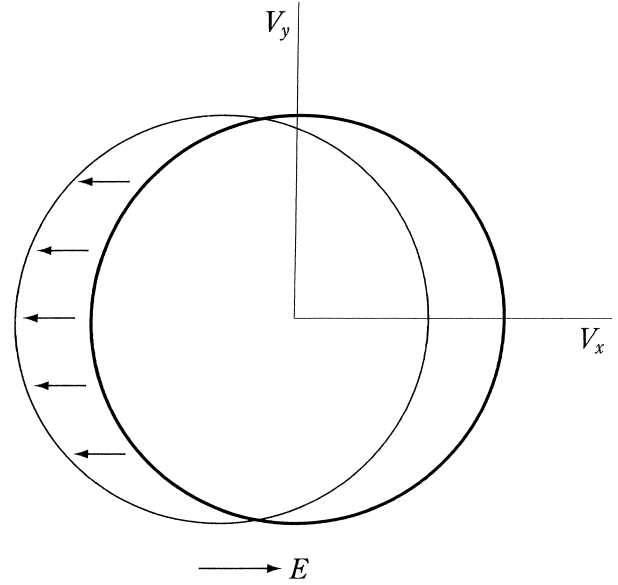


Fig. 3. Under an electric field the fermi sphere of a metal shifts to the direction opposite to the external electric field.

velocity antiparallel to  $\mathbf{E}$  increases (Fig. 3). Then a current parallel to  $\mathbf{E}$  flows and its magnitude increases in proportion to time. On the other hand, the direction of the velocity tends to be randomized by scattering of the electron, i. e., by the action represented by  $W_{\mathbf{k} \rightarrow \mathbf{k}'}$ . Then the situation that the velocity antiparallel to  $\mathbf{E}$  is leading is weakened and the tendency for the current to increase and that for the velocity randomized are balanced and finally the current becomes a constant and proportional to the electric field, thus ending in Ohm's law.

Now consider an electron well inside of the fermi sphere. It will be scattered to a state with the same energy, which will also be well inside of the fermi sphere because of the energy conservation. Such a state, however, will have already been occupied by an electron, so such scattering cannot take place. Then only the electrons in the energy range about  $k_B T$  around the fermi energy can make transition from impurity scattering and make contribution to the electrical resistance. This is because the states into which these electrons make transition may be empty (Fig. 2 (b)). Let the average of  $\gamma_{\mathbf{k}}$  for these electrons be  $\langle \gamma_{\mathbf{k}} \rangle$  and then the electrical resistivity is expressed by

$$\rho = m \langle \gamma_{\mathbf{k}} \rangle / n e^2, \quad [1]$$

here  $n$  is the density of the electrons.  $1/\langle \gamma_{\mathbf{k}} \rangle$  is called the relaxation time and represents the time during

which the electron with the wave number  $\mathbf{k}$  loses its wave number.

What is the temperature dependence of expression [1]? It arises from the fact that the average  $\langle\gamma_k\rangle$  is taken over the electrons in the energy range  $k_B T$  around the fermi energy. If  $\gamma_k$  depends very little on the electron energy,  $\langle\gamma_k\rangle$  will be nearly independent of the temperature. In fact the value of  $\gamma_k$  at the fermi energy and that apart from the fermi energy by 20 K will be almost the same. Then we expect  $\rho$  is nearly a constant around 20 K.

**3. Magnetic impurities.** In the previous discussion we supposed that metal copper contained a small amount of zinc impurity atoms. Now consider manganese as an impurity. In copper, valence of manganese will be +2 and manganese has five 3d electrons and their spins will be parallel due to Hund's rule. In Fig. 4(a) the energy levels of orbitals of  $Mn^{2+}$  are shown. For simplicity only one 3d orbital and one 3d electron are depicted. One might consider that the 3d orbital may admit one more electron with opposite spin (Fig. 4(b)). However, there occurs a large Coulomb energy  $U$  between two electrons in a 3d orbital.  $U$  is usually very large for 3d orbitals and the situation depicted in Fig. 4(c) will be realized. Then the electron which has an extra energy  $U$  may fall down to the fermi energy and the situation of Fig. 4(a) will occur again. This is the mechanism for the manganese ion to have a local spin (singly occupied 3d orbital). If  $U$  is small or 3d level is much lower, then the situation of Fig. 4(b) is stable. This is the case of zinc impurity. In this way whether the impurity atom has a local spin or not depends on the magnitude of  $U$ .

The valence of manganese ion is different from that of copper ion and so the free electron feels potential from the manganese impurities. This gives rise to the electrical resistance. In the case of manganese which possesses a local spin, however, there occurs another thing. The state of Fig. 4(a) is not a stationary state but may make transition to another state. Suppose that the electron with wave number  $\mathbf{k}$  and down spin jumps into the 3d orbital and the situation of Fig. 4(c) is realized. This process is possible virtually. By "virtually" I mean "for a short time". If after a short time the jumped electron returned to a state  $\mathbf{k}'$ , then the electron  $\mathbf{k}$  made transition to  $\mathbf{k}'$  effectively. When  $\mathbf{k}$  and  $\mathbf{k}'$  have the same energy, this transition is not virtual but real. This transition is possible when the 3d orbital is singly

occupied. The matrix element of this transition can be calculated and will be denoted as  $J(\mathbf{k} \rightarrow \mathbf{k}')$ . It is noted that the sign of  $J(\mathbf{k} \rightarrow \mathbf{k}')$  is negative. The rate of transition is obtained by taking its absolute square and then the electrical resistance is calculated as previously. The electrical resistance thus obtained is almost temperature independent for the same reason as in the previous case.

**4. Resistance minimum.** In the previous model of the magnetic impurity the free electron jumps into or out of the 3d orbital and an important factor is the Coulomb repulsion  $U$  which becomes effective when two electrons occupy a 3d orbital. This is a standard model for the magnetic impurity and is called the Anderson model,<sup>4)</sup> which is applicable not only to manganese but also to many other magnetic impurities. The electrical resistance calculated based on this model did not depend on the temperature very much, however. So let us take account of some correction to the calculation mentioned previously.<sup>3)</sup> The transition process considered in the previous section will be represented as  $\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}'\downarrow, \uparrow$  including spin, where the second arrow indicates the 3d spin. The matrix element of this process is denoted as

$$J(\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}'\downarrow, \uparrow). \quad [2]$$

However, the following process also gives us the same result  $\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}'\downarrow, \uparrow$ : Suppose the electron  $\mathbf{k}\downarrow$  virtually makes transition to  $\mathbf{k}''\downarrow$  and then to  $\mathbf{k}'\downarrow$ . Here  $\mathbf{k}''$  may have an energy different from  $\mathbf{k}$  but must not be occupied by an electron, otherwise such transition cannot occur due to Pauli's principle. This higher order process must be summed over  $\mathbf{k}''$ , and the quantum mechanics tells us that the matrix element is given by

$$\sum_{\mathbf{k}''} \frac{J(\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}''\downarrow, \uparrow) \cdot J(\mathbf{k}''\downarrow, \uparrow \rightarrow \mathbf{k}'\downarrow, \uparrow)}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}''}} (1 - f_{\mathbf{k}''}), \quad [3]$$

and the sum of [2] and [3] is the matrix element including the correction. Here  $\varepsilon_{\mathbf{k}}$  is the energy of the electron with wave number  $\mathbf{k}$  and from the relation  $\mathbf{k} = m\mathbf{v}/\hbar$  is expressed by  $\varepsilon_{\mathbf{k}} = m\mathbf{v}^2/2 = \hbar^2 \mathbf{k}^2/2m$ . The factor  $f_{\mathbf{k}}$  is unity when the state  $\mathbf{k}$  is occupied and zero when it is empty. Due to the factor  $1 - f_{\mathbf{k}''}$ , the summation in [3] is limited to the unoccupied states, namely to the outside of the fermi sphere.

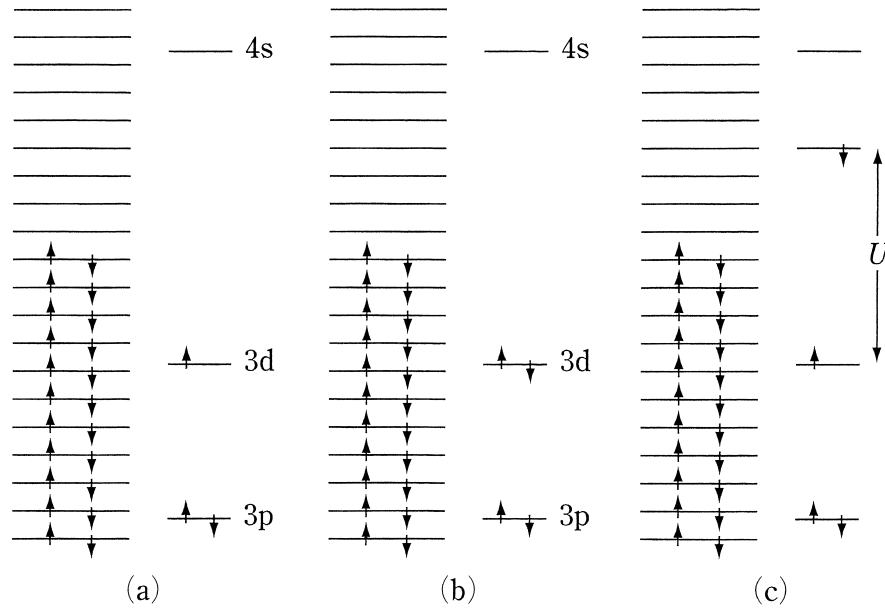


Fig. 4. Energy levels of the free electron in a metal and those of the impurity atom. (a) In a magnetic impurity a local spin exists in the 3d level. (b) The spin of the 3d level was canceled by the free electron. (c) An energy  $U$  is necessary for two electrons to occupy a single 3d level.

There is another higher order process which gives the same result as the above one. In this process an electron  $\mathbf{k}''\downarrow$  within the fermi sphere first makes transition to  $\mathbf{k}'\downarrow$  and then the electron  $\mathbf{k}\downarrow$  to  $\mathbf{k}''\downarrow$ . This also results in the transition  $\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}'\downarrow, \uparrow$ . In this case the summation over  $\mathbf{k}''$  is made within the fermi sphere. The matrix element of this process is expressed by

$$\sum_{\mathbf{k}''} \frac{J(\mathbf{k}''\downarrow, \uparrow \rightarrow \mathbf{k}'\downarrow, \uparrow) \cdot J(\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}''\downarrow, \uparrow)}{\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}''}} f_{\mathbf{k}''}, \quad [4]$$

which must be added to [3] to obtain the higher order matrix element. Now we note that in the real transition  $\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}'\downarrow, \uparrow$  the energy of the electron must be the same as before and after the transition, which implies  $\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}'}$ . When one adds [3] and [4] with this relation in mind, one finds the result

$$\sum_{\mathbf{k}''} \frac{J(\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}''\downarrow, \uparrow) \cdot J(\mathbf{k}''\downarrow, \uparrow \rightarrow \mathbf{k}'\downarrow, \uparrow)}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}''}}, \quad [5]$$

where the factor  $f_{\mathbf{k}''}$  has disappeared. Then the summation over  $\mathbf{k}''$  extends both inside and outside of the fermi sphere. The summation outside will be cut off at an appropriate energy.

To have a temperature dependence of the resistivity the transition rate  $\gamma_{\mathbf{k}}$  must be dependent

on the value of  $\mathbf{k}$ . Since [5] involves  $\varepsilon_{\mathbf{k}}$ , one has a  $\mathbf{k}$ -dependence of the transition rate. How big is the dependence? Since the numerator of [5] is not strongly dependent on  $\mathbf{k}''$ , we may consider it as a constant and take out of the summation sign:

$$J^2 \sum_{\mathbf{k}''} \frac{1}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}''}}.$$

Let us denote the number of  $\mathbf{k}''$  whose energy is between  $\varepsilon_{\mathbf{k}''}$  and  $\varepsilon_{\mathbf{k}''} + d\varepsilon_{\mathbf{k}''}$  by  $\rho(\varepsilon_{\mathbf{k}''})d\varepsilon_{\mathbf{k}''}$ , then the above sum may be written as

$$J^2 \int_0^D \frac{1}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}''}} \rho(\varepsilon_{\mathbf{k}''}) d\varepsilon_{\mathbf{k}''}.$$

Here the integral was cut at  $D$ , which may be a few times larger than the fermi energy. When  $\varepsilon_{\mathbf{k}''}$  is close to  $\varepsilon_{\mathbf{k}}$ , the integrand may be large. However, its sign changes when  $\varepsilon_{\mathbf{k}''}$  passes through  $\varepsilon_{\mathbf{k}}$ , and so the integral may not become large. In fact if  $\rho$  is set to a constant, the integral becomes  $J^2 \rho \log |\varepsilon_{\mathbf{k}}/(\varepsilon_{\mathbf{k}} - D)|$ , which is never large. One also sees that this expression is very weakly dependent on  $\mathbf{k}$ . The value of this expression for  $\varepsilon_{\mathbf{k}}$  equal to the fermi energy and that for  $\varepsilon_{\mathbf{k}}$  only slightly different from the fermi energy are almost the same, as one can immediately see from the expression. Then the electrical resis-

tivity calculated with this expression has only small temperature dependence.

Now we enter the main subject. In either the process [3] or [4] the direction of 3d spin remained the same. However, in the intermediate state the spin direction may be reversed. If first the transition  $\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}''\uparrow, \downarrow$  took place and then the transition  $\mathbf{k}''\uparrow, \downarrow \rightarrow \mathbf{k}'\downarrow, \uparrow$  followed, we eventually obtain the transition  $\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}'\downarrow, \uparrow$ , with the intermediate spin reversed. The matrix element of this process is expressed by

$$\sum_{\mathbf{k}''} \frac{J(\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}''\uparrow, \downarrow) \cdot J(\mathbf{k}''\uparrow, \downarrow \rightarrow \mathbf{k}'\downarrow, \uparrow)}{\varepsilon_k - \varepsilon_{k''}} (1 - f_{k''}), \quad [6]$$

which must be added to [5]. This involves the fermi factor  $f_{k''}$ . We have seen that the fermi factor in [3] was cancelled by that in [4]. One might consider that the same thing might happen for the fermi factor in [6]. For this one must consider the process where the order of the transition  $\mathbf{k}\downarrow, \uparrow \rightarrow \mathbf{k}''\uparrow, \downarrow$  and  $\mathbf{k}''\uparrow, \downarrow \rightarrow \mathbf{k}'\downarrow, \uparrow$  is reversed. However, it is impossible that  $\mathbf{k}''\uparrow \rightarrow \mathbf{k}'\downarrow$  takes place first, because the 3d spin is up first and so  $\mathbf{k}''\uparrow, \uparrow$  must make spin-flip transition but this is impossible. In order to estimate the value of [6] we note that the numerator and  $\rho(\varepsilon_{k''})$  do not depend on  $\mathbf{k}''$  strongly and we regard them constants. Then [6] becomes

$$J^2 \rho \int_0^D \frac{1 - f_{k''}}{\varepsilon_k - \varepsilon_{k''}} d\varepsilon_{k''} = J^2 \rho \int_{\varepsilon_F}^D \frac{1}{\varepsilon_k - \varepsilon_{k''}} d\varepsilon_{k''}. \quad [7]$$

Due to the factor  $1 - f_{k''}$  the integral over  $\varepsilon_{k''}$  is cut off at the fermi energy. This integral is evaluated easily and [7] becomes  $J^2 \rho \log |(\varepsilon_k - \varepsilon_F)/(\varepsilon_k - D)|$ . Adding this to the lowest order term  $J$  and taking its absolute square we find the transition rate from  $\mathbf{k}$  to  $\mathbf{k}'$  as

$$W_{\mathbf{k} \rightarrow \mathbf{k}'} \propto J^2 + 2J^3 \rho \log |(\varepsilon_k - \varepsilon_F)/(\varepsilon_k - D)| + O(J^4). \quad [8]$$

We note that  $\gamma_k$  is proportional to the same expression.

In previous works the electrical resistivity was calculated using the  $J^2$  term of [8]. The new term is of the order of  $J^3 \rho$  and about 1/10 of  $J^2$ . This is not small and depends on the electron energy strongly. In fact when  $\varepsilon_k$  is very close to  $\varepsilon_F$  the logarithm

tends to diverge. This is due to the fact that the lower limit of integration is  $\varepsilon_F$  and this fact is due to the factor  $1 - f_{k''}$  in [6]. The same factor was in [3], which was cancelled by another factor in [4]. On the other hand such cancellation did not occur for [6].

According to [1] the electrical resistivity is obtained by averaging  $\gamma_k$  over the electron energy  $\varepsilon_k$  in the range about  $k_B T$  around  $\varepsilon_F$ , thus it is expressed by

$$R = R_0 [1 + 2J\rho \log |k_B T / (D - \varepsilon_F)|], \quad [9]$$

where  $R_0$  is the resistivity obtained when  $J^2$  in [8] is used and  $D - \varepsilon_F \gg k_B T$  was assumed. Since  $J$  is considered to be negative, the resistivity of [9] increases logarithmically as the temperature is decreased. This is experimentally observed and an example is shown in Fig. 5.<sup>3)</sup>

Now we mention how the difficulties mentioned at the begining were overcome. First, we took the Anderson model, which is very universal and may be applicable to all the magnetic impurities. Second, the increase of the resistivity following decrease of the temperature is explained by a negative  $J$ . That  $J$  is negative can be shown from the derivation of the matrix element. Third, the temperature dependence of the resistivity at very low temperature is understood from the logarithmic correction term. This temperature dependence does not come from the impurity itself but comes from the free electrons. When the electron energy  $\varepsilon_k$  is close to  $\varepsilon_F$ , the transition rate diverges logarithmically.

We have seen that [9] agrees with experiment very well. However, it involves a difficulty that the resistivity diverges as the temperature  $T$  approaches zero. Actually before the zero temperature, as the temperature defined by

$$k_B T_K \equiv (D - \varepsilon_F) e^{1/J\rho} \quad [10]$$

is approached, the second term of [9] becomes comparable to the first term and no more a correction term, so [9] is not valid below this temperature. This problem has been treated by many people. According to these works higher order terms are important. [8] or [9] involves the first two terms in the expansion in terms of  $J\rho$ . The terms higher than these involve higher powers of  $\log T$  and all become comparable at  $T_K$ , so expansion must include all these terms. According to these calculations the resistivity deviates from  $\log T$  below  $T_K$  and approaches a constant. According to [10]  $T_K$  depends on  $J\rho$  sensitively and may

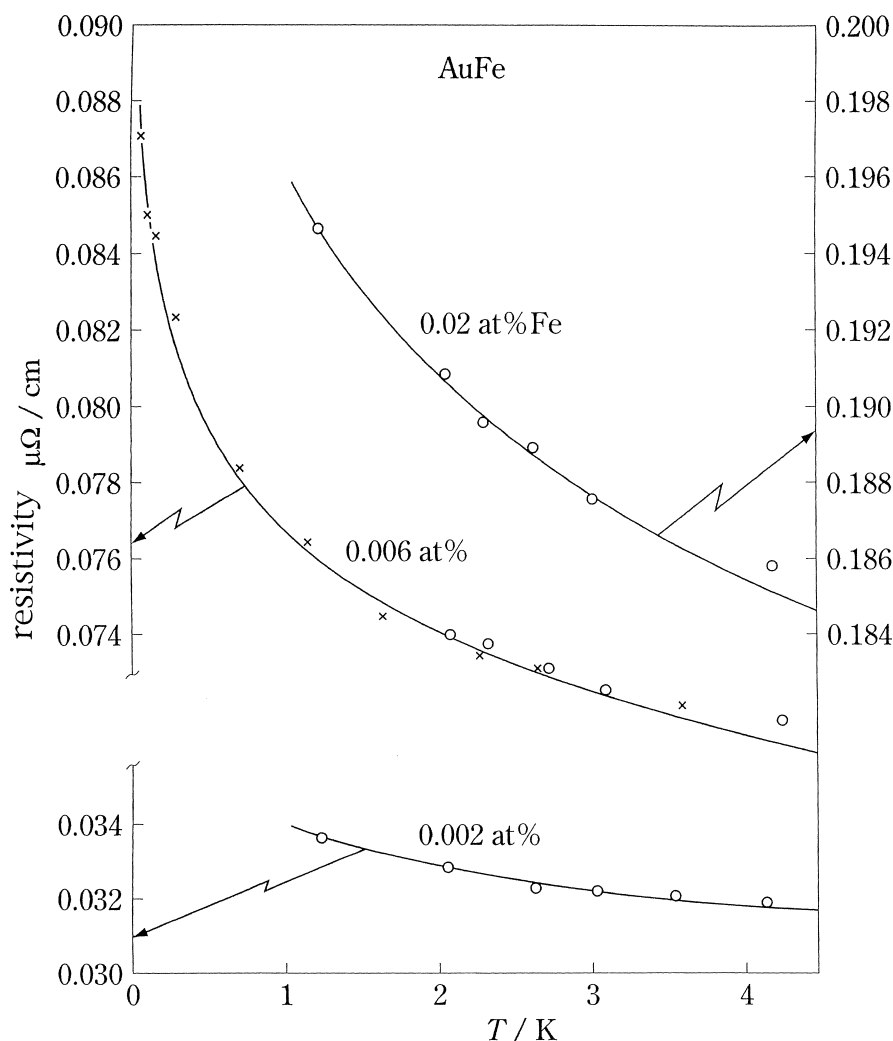


Fig. 5. The temperature dependence of the resistivity of gold with small amount of iron impurity. Comparison between theory and experiment.

take various values depending on the host metal and the impurity, being higher than 100 K for some alloy and lower than 0.01 K for other. For alloys with higher  $T_K$  the resistivity is experimentally observed to approach a constant.

**5. Later development.** With resistance minimum as a start, the magnetic impurity in the metal interested many people theoretically and experimentally.<sup>5)</sup> The central issue is the interaction between the free electron of the metal and the impurity with local spin. In this paper it was represented by  $J$ . If this is zero, both systems are independent

and the impurity has a local spin and shows a Curie susceptibility. If  $S = 1/2$ , the spin is doubly degenerate and may be up or down and one mol of the spin has an entropy  $R \ln 2$ . If  $J$  is finite, the free electron is scattered and the spin direction of the impurity may be changed. These facts have an effect on the susceptibility and the entropy. When these quantities are expanded in terms of  $J$ , one has  $\log T$  terms. As a result of this the susceptibility deviates from the Curie law below  $T_K$  and tends to a constant as absolute zero of temperature is approached. Furthermore the entropy tends to decrease below  $T_K$  and the specific heat shows a peak. As the absolute zero is approached, the specific heat per spin tends to zero following the law  $k_B T/T_K$ .

\*) This is applicable only in quantum world. In classical physics a precise measurement will give us  $\Delta\nu \approx 0$  even when  $t$  is shorter than  $T$ .

The properties of the magnetic impurity in metals change drastically at  $T_K$ . What happens at  $T_K$ ? We note that the change at  $T_K$  is not discontinuous but gradual. The key fact is that the spin direction of the impurity changes due to the interaction. The change occurs according to the following process. The electron with down spin interacts with the up spin of the impurity and flips its spin downward and at the same time flips the electron spin itself upward. The upward flip of the impurity spin may be considered in a similar way. This is quite similar to the nuclear spin in metals interacting with metallic electrons and flipping its own spin. The mechanism of this spin flip is called the Korringa mechanism and is familiar to NMR people. By a calculation similar to this case the rate of the spin flip is obtained as

$$\Gamma = (2\pi/\hbar)J^2\rho^2k_BT. \quad [11]$$

The inverse of this is the time during which the spin flips and is called the relaxation time  $\tau$ :

$$\tau = (\hbar/2\pi J^2\rho^2k_BT). \quad [12]$$

$J$  and  $\rho$  here may be considered to be the same as those of previous sections.

When  $\Gamma$  is very large ( $\tau$  short), the spin flips up and down quickly and is half up and half down (case 1). On the other hand when  $\Gamma$  is very small ( $\tau$  long), the spin may be either up or down (case 2). Physics shown by the spin may be quite different in these two cases, and we note that  $T_K$  indicates the distinction between the two cases. This will be discussed later, but at present we shall tell that  $\Gamma$  is large when  $\hbar\Gamma \gg k_BT$  (case 1) and vice versa. Why the temperature comes in here will be explained later.

Before telling this we mention about the uncertainty relation between time and energy. We present a very naive explanation of this. Suppose we observe an oscillator for the time  $t$  and want to find its frequency. If  $t$  is very large compared with the period  $T$  of the oscillation, the frequency will be determined very accurately. Let the frequency be  $\nu$  and its error  $\Delta\nu$ , then we will have  $\Delta\nu/\nu \approx T/t$ .<sup>\*)</sup> Noting  $\nu T = 1$  and multiplying both sides of this expression by the Planck constant  $h$ , we have  $\Delta(h\nu) \approx h/t$ .  $h\nu$  is the energy  $E$  of the oscillator, but may in general be taken as the energy:

$$t \approx h/\Delta E. \quad [13]$$

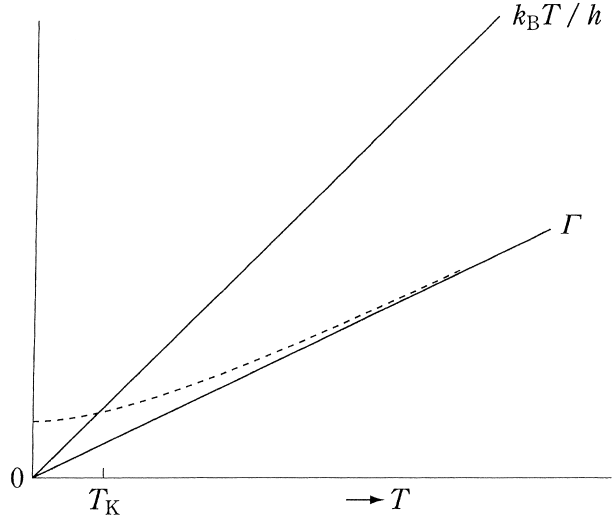


Fig. 6. Relation between  $\Gamma$  and  $T$  given by [11].  $\Gamma$  actually behaves as a dotted line and exceeds  $k_BT/h$  below  $T_K$ .

This is the uncertainty relation between time and energy. This relation is interpreted as follows: When one knows the energy of a system with the accuracy  $\Delta E$ , he observes the system for time  $t$  given by [13].

Going back to the temperature, let us assume that the magnetic impurity is at the temperature  $T$ . Then the impurity receives an energy of the order of  $k_BT$ , which may actually be  $2k_BT$  or  $0.5k_BT$ . In any case uncertainty of the energy is about  $k_BT$ . Then [13] tells us that we observe this system only for the time  $h/k_BT$ . Comparing this time with the spin relaxation time  $\tau$  [12] we find  $\tau \gg h/k_BT$  because of  $J^2\rho^2 \ll 1$ . This means that the spin relaxation time is much longer than the time for which we observe the system. When we see the spin, it may be either up or down and does not change its direction quickly. In another word the spin is doubly degenerate. This is the base for calculations of [3] and [6] etc. and corresponds to the case of  $T > T_K$ .

This argument becomes invalid when the temperature becomes lower than  $T_K$ . This is because the expression of  $\tau$  [12] or  $\Gamma$  [11] becomes invalid at low temperatures. For example [11] is the lowest order of  $J$ . Higher order terms involve  $\log T$  and  $\Gamma$  ceases decreasing in proportion to  $T$  and becomes  $\Gamma \approx k_BT_K/h$  at  $T_K$  and tends to a constant as  $T \rightarrow 0$  (Fig. 6). Consequently  $\tau$  ceases increasing in proportion to  $T^{-1}$  below  $T_K$  and tends to a constant. As a result of this we have  $\tau < h/k_BT$  below  $T_K$ . Namely, below  $T_K$  the spin changes its direction for much shorter time than the time for which we ob-



serve the spin. Then the up spin state and the down spin state will be mixed and double degeneracy will be removed. The susceptibility will deviate from the Curie law and will approach the Pauli susceptibility. The entropy tends to zero as  $T \rightarrow 0$ . In this way physics of the magnetic impurity drastically changes across  $T_K$ .

We shall mention the electrical resistivity. We will use Friedel's theorem, according to which the electrical resistivity caused by an impurity is small when the number of electrons in the orbital of the impurity is 0 or 1 and large when it is  $1/2$ . Then above  $T_K$  the spin direction is either up or down and the number of up spin electron is 1 and that of down spin electron is 0 or vice versa and so anyway the resistivity is small. Below  $T_K$  the spin is half up and half down and so the number of each electron is  $1/2$  and the resistivity is large. Consequently, as the temperature goes down, the resistivity increases across  $T_K$ . The  $\log T$  term which appeared in the resistivity at high temperature is the initiative of this increase.

**6. Heavy fermions.** Up to now we have assumed that the concentration of the impurity is small (for example, less than 1%). Then the interaction between impurities will be neglected, and in fact the resistivity due to impurities is known experimentally to be proportional to the impurity concentration. For higher impurity concentration we have a different situation. There occurs an RKKY interaction<sup>\*\*)</sup>  between impurity spins, which may be positive or negative depending on the distance between the impurities and so acts so as to align the spins parallel or antiparallel. As a result the spin may be aligned to some direction determined by other spins. Since the impurities are randomly distributed, the spin arrangement will not be regular such as ferromagnetism or antiferromagnetism but will be such that called a spin glass. At high temperatures the spin directions will be thermally randomized and the spins become paramagnetic. If the temperature at which such paramagnetic transition occurs is denoted by  $T_m$ , then  $k_B T_m$  is of the order of the interaction energy between the spins and is small when the impurity concentration is small.  $T_m$  is the temperature at which the spin directions are fixed by the spin-spin interaction. When the spin direction is fixed,

the resistance minimum is not seen. This is because, as mentioned previously, the  $\log T$  term comes from spin flip in the intermediate state. In previous sections we have been assuming that  $T_m$  is much lower than  $T_K$ . In this case there happens nothing new when the temperature becomes lower than  $T_m \ll T_K$ . When the temperature is lower than  $T_K$ , the spins are half up and half down and this state gives rise to a gain of the energy of the order of  $k_B T_K$ . Since this is much larger than the spin-spin interaction  $\approx k_B T_m$ , the spin state will not be affected by the spin-spin interaction very much.

On the other hand when the impurity concentration is large and  $T_m$  is higher than  $T_K$ , the system first becomes spin glass. When the temperature is lowered to  $T_K$ , there occurs nothing new just as in the previous case. Since the spins are fixed, spin flip is not possible to give rise to the resistance minimum. The electrical resistivity shows a complicated temperature dependence for spin glass. Spin glass behavior is seen when, for example, copper contains more than 1% of manganese.

Recently substances were discovered where  $T_m$  never exceeds  $T_K$  even at high concentration of the impurity. This can happen when  $T_K$  is intrinsically high and the spin-spin interaction is small. We mention a typical example of these substances.  $\text{LaCu}_6$  is a usual metal and La can be 100% replaced by Ce. The compound  $\text{Ce}_x\text{La}_{1-x}\text{Cu}_6$  takes the same crystal structure for  $0 \leq x \leq 1$  and Ce has a single f electron and so has a magnetic moment. Then one may imagine that at  $x = 1$  the Ce spins may show some kind of magnetic order, such as ferromagnetism or so. The temperature dependence of the resistivity of this system is shown in Fig. 7.<sup>6)</sup> One sees a resistance minimum at 9.4% of Ce and at more concentration of Ce. For concentration more than 50% one sees a maximum in the resistivity curve below the temperature of the resistance minimum. Surprisingly one sees a resistance minimum even at 100% of Ce. This means that the spins are not fixed nor ordered even at this concentration, otherwise the resistance minimum would not occur. Above  $T_K$  the spins are randomly up or down and this randomness causes the electrical resistivity. As the temperature goes down through  $T_K$ , all the spins will be half up and half down. Since all the spins are now in the same state, there is no randomness at all for 100% Ce and we expect the resistivity finally goes to zero as the temperature goes to zero. We can see this in Fig. 7.

<sup>\*\*)</sup>  RKKY interaction is an indirect interaction between two spins embedded in a metal mediated by the free electrons of the metal.

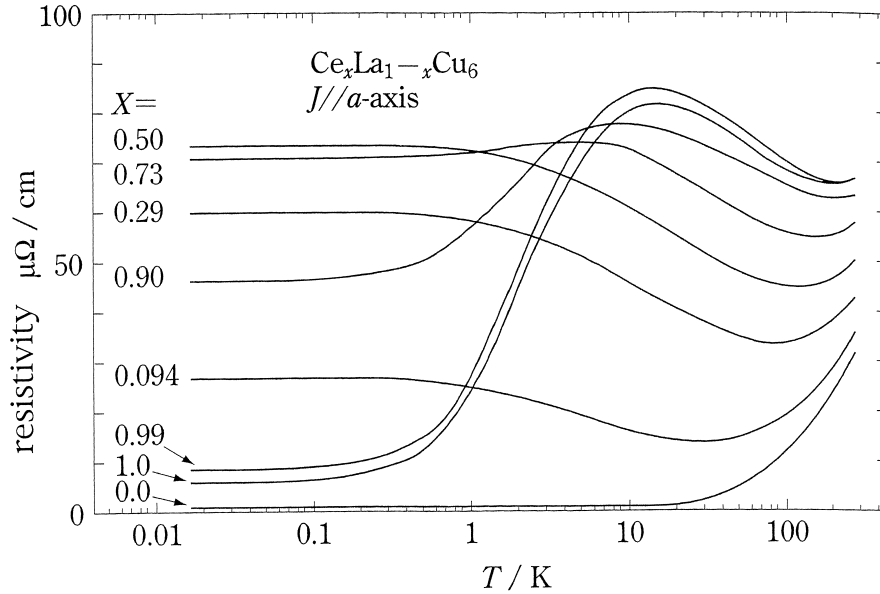


Fig. 7. Temperature dependence of the electrical resistivity of  $\text{Ce}_x\text{La}_{1-x}\text{Cu}_6$ . Resistance minimum is seen for all  $x > 0$  and a maximum is also seen for  $x > 0.5$ .

In this compound  $T_m$  is lower than  $T_K$  for two reasons. First, the 4f orbital of Ce is singly occupied and the spin of Ce is  $1/2$ . The spin-spin interaction is proportional to the square of the spin and so is small. Second, the 4f orbital is sevenfold degenerate and it is shown that  $T_K$  is high for degenerate orbitals. If two 4f electrons are present, the effect of degeneracy is weakened and  $T_K$  will not become high. For this reason high  $T_K$  is expected for Ce and Yb. In the latter case the hole is sevenfold degenerate. In fact the case of  $T_K$  higher than  $T_m$  is commonly found in the intermetallic compounds of Ce and Yb.

Another interesting feature of these substances is the specific heat. As was mentioned in section 5, the specific heat of the magnetic impurity below  $T_K$  tends to zero as  $k_B T/T_K$ . If the impurities can be regarded as isolated even for very high impurity concentration, then the specific heat should go as  $k_B T/T_K$  multiplied by the number of the magnetic impurities. For one mole of the magnetic impurities this becomes  $RT/T_K$  ( $R$  is the specific gas constant), which is very large. The molar electronic specific heat of ordinary metals is of the order of  $R(k_B T/\varepsilon_F)$ , where  $\varepsilon_F$  is the fermi energy of the metal and is usually about 5 eV or 50000 K. On the other hand  $T_K$  is several tens degrees Kelvin at most and so  $RT/T_K$  is about 1000 times larger than the electronic specific heat of ordinary metals. Many substances which

show such a large specific heat have been discovered among Ce compounds. In the case of  $\text{CeCu}_6$  the coefficient of  $T$  of the molar specific heat is  $1.5 \text{ J/molK}^2$  and very large.

The fermi energy  $\varepsilon_F$  of a metal is inversely proportional to the effective mass of the electron in the metal and if one is going to interpret such a large specific heat in terms of  $R(k_B T/\varepsilon_F)$ , one can consider that the effective mass of the electron in the substance is about 1000 times larger than the mass of the electron. In this sense these substances are called heavy fermion systems. They are a new substance and show resistance minimum at high temperatures and the atoms like Ce seem to have magnetic moments. But at low temperatures they do not show any magnetic order and spins of Ce look to have disappeared and they show a very large electronic specific heat at low temperatures.

**7. Conclusion.** In this paper we first mentioned the theory of the resistance minimum for metals involving magnetic impurities. It explained why the resistivity arising from the magnetic impurity increases as the temperature goes down. In calculating electrical resistivity quantum mechanically it is necessary to find the matrix element of the transition for the electron to jump from the initial state to the final state. If this matrix element depends on the energy of the electron of the initial state, one obtains a

temperature dependence of the resistivity. When the matrix element was calculated in the lowest approximation as usually done, the temperature dependence was not obtained. So we considered higher order process where the final state was reached via an intermediate state from the initial state. We found that the energy dependence of the matrix element is obtained when we take account of the process where the spin of the magnetic impurity is reversed in the intermediate state. From this energy dependence a  $\log T$  dependence of the resistivity was derived and a good agreement with experiments was obtained.

When the temperature goes lower than  $T_K$ , the correction term becomes of the same order of the first term and higher order terms are needed and physics changes drastically across  $T_K$ . Above  $T_K$  the impurity spin is either up or down and changes its direction occasionally. This is the magnetic state and the susceptibility increases following Curie's law as the temperature goes down and the resistivity shows the  $\log T$  dependence. Below  $T_K$  the spin direction changes rapidly and the spin is in a state of superposition of up and down spin states. The resistivity and the susceptibility tend to a constant as the temperature goes to zero.

## Profile

Jun Kondo was born in Tokyo in 1930. After graduating from the Faculty of Science at the University of Tokyo, he entered the doctor course in physics at the University of Tokyo and obtained his Ph. D. for the work "Superexchange Interaction in MnO". Then he became a research assistant at the Institute of Solid State Physics in 1960 and worked on the anomalous Hall effect in ferromagnetic metals. He took a model where the magnetic electrons are localized and considered scattering of the conduction electrons off the localized magnetic electrons and obtained a skew scattering of the conduction electrons. Thus he was able to explain the anomalous Hall effect of Fe and Ni quite well. He moved to Electrotechnical Laboratory in 1963 and worked on the resistance minimum of dilute magnetic alloys. He calculated the scattering rate of the conduction electrons off the localized magnetic impurity beyond the first Born approximation. He found that the resistivity of the alloy involves a term proportional to the logarithm of the temperature and could explain the experimental data quite well. His later work involves the muon tunneling in metals. He calculated the rate of the tunneling of the muon between neighbouring interstitial sites. He found that the rate is proportional to a power of the temperature, which agreed with experimental findings. He was awarded the Nishina Memorial Prize in 1968, the Imperial Prize and Japan Academy Prize in 1973, the Asahi Prize in 1979, the Fujiwara Prize in 1984, the Fritz London Memorial Prize in 1987 and the Acta Metallurgica Gold Medal in 1992. He was elected a member of the Japan Academy in 1997.

The above story is for the case of small concentration of impurities. In contrast to this case a new kind of compounds, mainly Ce compounds, was discovered where the interaction between magnetic atoms is very small and the atoms behave as are isolated from other atoms, even for 100% magnetic atoms. These compounds have an electronic specific heat which is, in some cases, 1000 times larger than that of ordinary metals. These are called heavy fermion systems and are actively studied as a new substance.

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