

occurs for each alloy at about 600°K, above which (according to earlier measurements up to 1270°K by Schüle and Kehr⁶) the resistivity continues to rise monotonically.

The change in resistivity in the 200-600°K region could be interpreted as a sum of two contributions: an increasing term due to phonon scattering, and a decreasing term due to spin-disorder scattering from the local moment clouds. Since the latter can be expected to vary as some simple direct function of the moment, it seems reasonable to interpret the data as indicating that the effective paramagnetic moment of each cloud is smoothly decreasing to zero as the temperature rises to 600°K. Whether the structure in the data below 50°K for the paramagnetic alloys represents an additional effect, such as Kondo scattering, or an anomalous change of the moment per cloud, cannot be determined at this time. The low-temperature behavior of the ferromagnetic alloys can clearly be interpreted as the freezing out of spin-disorder scattering.

The fact that the spin-disorder scattering disappears at about 600°K, independent of alloy composition, indicates that the giant polarization clouds persist up to a temperature near the

Curie point of nickel (approximately 625°K). This suggests that within a statistical Ni-rich local region which is the nucleating site of a magnetic polarization cloud in Ni-Cu,² the exchange forces are quite comparable in strength with those in pure nickel.

A detailed interpretation of the resistivity below 600°K has not been possible to date. Additional measurements on Ni-Cu alloys with lower Ni content will be made in an effort to extract the magnetic-scattering contribution to the resistivity.

*Work supported by the Office of Aerospace Research, U. S. Air Force Office of Scientific Research, under Grant No. AFOSR 894-67.

¹T. J. Hicks, B. Rainford, J. S. Kouvel, G. G. Low, and J. B. Comly, *Phys. Rev. Lett.* **22**, 531 (1969).

²J. S. Kouvel and J. B. Comly, *Phys. Rev. Lett.* **24**, 598 (1970).

³T. Skoskiewicz and B. Baranowski, *Solid State Commun.* **7**, 647 (1969).

⁴R. W. Houghton, M. P. Sarachik, and J. S. Kouvel, to be published.

⁵J. Crangle and P. J. L. Butcher, to be published.

⁶W. Schüle and H. P. Kehr, *Z. Metallk.* **52**, 168 (1961).

KONDO SIDEBANDS

F. E. Maranzana

Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven, The Netherlands

(Received 6 April 1970)

Logarithmic resonances away from the Fermi level are obtained when the magnetic ion of the *s-d* model is subject to a crystal field. Indications exist that such resonances are observed in the resistivity-versus-temperature curve of CeAl₃.

Recently a number of experimental results have been published¹⁻³ concerning the behavior as a function of temperature of the resistivity of several intermetallic compounds containing cerium. Some puzzling aspects of these measurements have stimulated the effort whose results are to be reported presently.

A variation of the *s-d* model has been considered. The system consists of a gas of charge carriers and of a periodic array of spins [these "localized" spins (*S*) in reality are the total angular momenta (*J*) of the Ce atoms]. The assumption is made that there exists no correlation between the motion of any two spins. This assumption is valid in the paramagnetic region of the system, when the molecular-field approximation is adopted. Under these conditions each localized spin scatters the charge carriers independently and the fact that a periodic array of spins exists is irrelevant in what follows. Periodicity plays, on the contrary, an important role if these considerations are extended to the ordered phase of the system.⁴ This extension is not included in the present Letter.

Each localized spin has $S = \frac{5}{2}$ (the calculation is to be applied to Ce ions); the six energy levels E_m ($m = 1, 2, \dots, 6$) of the spin are split by a hexagonal crystal field into three doublets (this assumption applies to CeAl₃). The doublet states are eigenstates of the spin components S_z if the crystal-field *z* axis is chosen as the axis of quantization. An acceptable sequence of levels is the following: The $\pm \frac{5}{2}$ doublet lies lowest; above it, at an energy distance ΔE , the $\pm \frac{3}{2}$ doublet is to be found, while the

$\pm \frac{1}{2}$ doublet is highest.⁵

The charge carriers are assumed to reside in a band extending from $-E_1$ to E_1 , where the Fermi level $E_F = 0$ has been chosen as the zero of energy. This band has a constant density of states $n(E_F)$. The subsystem of localized spins is in the paramagnetic state so that the charge carriers with spin up and the charge carriers with spin down reside in the same band. The charge carriers and the spins interact by means of the well known s - d interaction⁶:

$$H = -\frac{J}{N} \sum_{kk'n} \exp[i(\vec{k}-\vec{k}') \cdot \vec{R}_n] \{S_{nz}(a_{k'\uparrow}^\dagger a_{k\uparrow} - a_{k'\downarrow}^\dagger a_{k\downarrow}) + S_{n+} a_{k'\downarrow}^\dagger a_{k\uparrow} + S_{n-} a_{k'\uparrow}^\dagger a_{k\downarrow}\}. \quad (1)$$

The quantity whose behavior is of interest here is the relaxation time τ_k of the charge carriers as a function of the energy E_k of the carrier. Carriers with opposite spins have equal relaxation times, because the periodic array of spins is paramagnetic.

An equation for the inverse of the relaxation time has been obtained by van Peski-Tinbergen and Dekker.⁷ This equation is

$$\frac{1}{\tau_k} = \sum_{k'} \left\{ 1 - f_k^0 \left[1 - \exp\left(\frac{E_k - E_{k'}}{k_B T}\right) \right] \right\}^{-1} \left(1 - \frac{|k'|}{|k|} \right) [W(k \uparrow \rightarrow k' \uparrow) + W(k \uparrow \rightarrow k' \downarrow)]. \quad (2)$$

f_k^0 is the equilibrium distribution of electrons, E_k and $E_{k'}$ are the energies of electron states of wave vector k and k' , respectively, the W 's are transition probabilities for an electron to be scattered, for instance, from a state of wave vector k and spin up to a state of wave vector k' and spin up. If the W 's are isotropic, the part of the summation over k' proportional to $|k'|/|k|$ vanishes upon integration.

The transition probabilities for the model under consideration have been calculated by means of perturbation theory limited to terms cubic in the coupling constant J . The transition probability $W^{(1)}$ which is quadratic in J is not essential for the present argument, and it will not be given explicitly. The transition probabilities $W^{(2)}(k \uparrow \rightarrow k' \uparrow)$ and $W^{(2)}(k \uparrow \rightarrow k' \downarrow)$ follow. They are cubic in J :

$$\begin{aligned} W^{(2)}(k \uparrow \rightarrow k' \uparrow) = & \frac{2\pi}{\hbar} \delta(E_k - E_{k'} + E_m - E_{m'}) \left(\frac{-J}{N}\right)^3 N \left\{ \sum_{k''m''} \left[\frac{1 - f_{k''}^0}{E_k - E_{k''} + E_m - E_{m''} + i\eta} + \text{c.c.} \right] \right. \\ & \times [\langle E_{m''} | S_z | E_m \rangle \langle E_{m'} | S_z | E_{m''} \rangle \langle E_m | S_z | E_{m'} \rangle + \langle E_{m''} | S_+ | E_m \rangle \langle E_{m'} | S_- | E_{m''} \rangle \langle E_m | S_z | E_{m'} \rangle] \\ & - \sum_{k''m''} \left[\frac{f_{k''}^0}{E_{k''} - E_{k'} + E_m - E_{m''} + i\eta} + \text{c.c.} \right] [\langle E_{m''} | S_z | E_m \rangle \langle E_{m'} | S_z | E_{m''} \rangle \langle E_m | S_z | E_{m'} \rangle \\ & \left. + \langle E_{m''} | S_- | E_m \rangle \langle E_{m'} | S_+ | E_{m''} \rangle \langle E_m | S_z | E_{m'} \rangle \right] \Big\}, \quad (3) \end{aligned}$$

and

$$\begin{aligned} W^{(2)}(k \uparrow \rightarrow k' \downarrow) = & \frac{2\pi}{\hbar} \delta(E_k - E_{k'} + E_m - E_{m'}) \left(\frac{-J}{N}\right)^3 N \left\{ \sum_{k''m''} \left[\frac{1 - f_{k''}^0}{E_k - E_{k''} + E_m - E_{m''} + i\eta} + \text{c.c.} \right] \right. \\ & \times [\langle E_{m''} | S_z | E_m \rangle \langle E_{m'} | S_+ | E_{m''} \rangle \langle E_m | S_- | E_{m'} \rangle - \langle E_{m''} | S_+ | E_m \rangle \langle E_{m'} | S_z | E_{m''} \rangle \langle E_m | S_- | E_{m'} \rangle] \\ & - \sum_{k''m''} \left[\frac{f_{k''}^0}{E_{k''} - E_{k'} + E_m - E_{m''} + i\eta} + \text{c.c.} \right] [\langle E_{m''} | S_+ | E_m \rangle \langle E_{m'} | S_z | E_{m''} \rangle \langle E_m | S_- | E_{m'} \rangle \\ & \left. - \langle E_{m''} | S_z | E_m \rangle \langle E_{m'} | S_+ | E_{m''} \rangle \langle E_m | S_- | E_{m'} \rangle \right] \Big\}. \quad (4) \end{aligned}$$

Equations (3) and (4) are sums of the four contributions from the four processes that can bring an electron from state k to state k' through one intermediate state. In either (3) or (4) the first two terms refer to processes in which the electron is scattered from k to k'' and finally to k' . The two remaining terms, on the other hand, are typical Kondo processes in which two electrons are involved, first an electron being scattered from k'' to k' and then another electron being scattered from k to k'' . In (3) and (4) the occupation number $f_{k''}^0$ of the intermediate state is of course involved. The essential difference between the present equations and the corresponding ones obtained by Kondo resides in the presence in the denominators in (3) and (4) of the differences between two energy levels of the scattering spin. These extra addends shift the value of $E_{k''}$ at which the sum over k'' is divergent, away from

the Fermi level.

When $T=0$ in (3) and (4) the sum over k'' can be performed in closed form. The usual logarithmic terms are the result of the step-function character of f^0 . The arguments of these logarithms contain, of course, the energy differences between two levels of the localized spin. Moreover a sum over the final states $E_{m'}$ is performed and an average over the initial states E_m . The transition probabilities thus obtained are substituted in (2), and the following result is arrived at:

$$1/\tau_k = 1/\tau_k^{(1)} + 1/\tau_k^{(2)}; \quad (5)$$

$$\begin{aligned} \frac{1}{\tau_k^{(2)}} = & \frac{2\pi}{\hbar} \left(\frac{-J}{N} \right)^3 N n^2(E_F) \left[\sum_m \exp\left(\frac{-E_m}{k_B T}\right) \right]^{-1} \left\{ \sum_{mm'm''} \left[(1-f_k^0) \exp\left(\frac{E_m}{k_B T}\right) + f_k^0 \exp\left(\frac{E_{m'}}{k_B T}\right) \right]^{-1} \right. \\ & \times \left[\ln \left| \frac{E_k + E_m - E_{m'}}{E_1} \right| \langle E_m | S_z | E_{m'} \rangle \langle E_{m''} | S_z | E_m \rangle \langle E_{m'} | S_z | E_{m''} \rangle + \langle E_{m''} | S_+ | E_m \rangle \langle E_{m'} | S_- | E_{m''} \rangle \right) \\ & - \ln \left| \frac{E_k + E_{m'} - E_m}{E_1} \right| \langle E_m | S_z | E_{m'} \rangle \langle E_{m''} | S_z | E_m \rangle \langle E_{m'} | S_z | E_{m''} \rangle + \langle E_{m''} | S_- | E_m \rangle \langle E_{m'} | S_+ | E_{m''} \rangle \right) \\ & \left. + \ln \left| \frac{E_k + E_m - E_{m'}}{E_1} \right| + \ln \left| \frac{E_k + E_{m'} - E_m}{E_1} \right| \langle E_m | S_- | E_{m'} \rangle \langle E_{m''} | S_z | E_m \rangle \langle E_{m'} | S_+ | E_{m''} \rangle \right. \\ & \left. - \langle E_{m''} | S_+ | E_m \rangle \langle E_{m'} | S_z | E_{m''} \rangle \right\}. \quad (6) \end{aligned}$$

$1/\tau_k^{(1)}$ is the contribution proportional to J^2 resulting from the first Born approximation. This contribution is irrelevant in the present context. Attention will rather be focused on Eq. (6). The symmetry of this equation under exchange of electrons and holes should be emphasized. Equation (6) reduces to the well-known expression obtained by Kondo⁶ in the limit of zero crystal field; then only a logarithmic divergence is obtained at the Fermi level. If however the crystal field is finite, a number of side divergences appear. Equation (6) reduces to

$$\frac{1}{\tau_k^{(2)}} \propto \frac{25}{4} \left(\ln \left| \frac{E_k + \Delta E}{E_1} \right| + \ln \left| \frac{E_k - \Delta E}{E_1} \right| \right), \quad |E_k| < \Delta E; \quad (7)$$

$$\frac{1}{\tau_k^{(2)}} \propto \frac{5}{2} \ln \left| \frac{E_k}{E_1} \right| + \frac{25}{4} \ln \left| \frac{E_k + \Delta E}{E_1} \right| + \frac{35}{4} \ln \left| \frac{E_k - \Delta E}{E_1} \right|, \quad E_k > \Delta E; \quad (8)$$

$$\frac{1}{\tau_k^{(2)}} \propto \frac{5}{2} \ln \left| \frac{E_k}{E_1} \right| + \frac{25}{4} \ln \left| \frac{E_k - \Delta E}{E_1} \right| + \frac{35}{4} \ln \left| \frac{E_k + \Delta E}{E_1} \right|, \quad E_k < -\Delta E. \quad (9)$$

It should be recalled that Eqs. (7), (8), and (9) apply only at $T=0$. At this temperature all localized spins are in the lowest doublet state, $\pm \frac{5}{2}$. Scattering to the $\pm \frac{1}{2}$ doublet is impossible, so that only the $\pm \frac{3}{2}$ doublet is accessible at $T=0$. For this reason only ΔE appears in the formulas and the distance between the $\pm \frac{5}{2}$ and the $\pm \frac{1}{2}$ doublets is irrelevant.

The behavior of $1/\tau_k^{(2)}$ as a function of E_k has been plotted in Fig. 1. The most remarkable aspect of the relaxation time at $T=0$ is the fact that no logarithmic divergence appears for $E_k=0$. Indeed, in the present model ($m = \pm \frac{5}{2}$ is the ground state) when $T=0$ no spin-flip scattering is possible without energy expenditure. The Kondo effect is suppressed at $E_k=0$ and it is shifted to that energy value for which the localized spin can resonate with spin-flipping electrons.

In view of the fact that the present calculation is a perturbation calculation, it is obviously

quite premature to take the above indications seriously enough to attempt a comparison with experiment. One might, however, be willing to speculate on the consequences of the possible existence of these logarithmic divergences at finite E_k . In the first place one should not expect a logarithmic divergence in the curve of ρ vs T as $T \rightarrow 0$. In fact the Kondo divergence at $E_k=0$ has disappeared in Eq. (7); the relaxation time $1/\tau_k^{(2)}$ decreases as $E_k \rightarrow 0$. On the other hand, as the temperature increases and the charge carriers begin to occupy states of energy $E_k \simeq \Delta E$ the resistivity increases because many electrons are scattered resonantly. At very high temperatures the charge carriers are distributed uniformly in k space, and only a very small fraction has the resonance energy. One expects then one or more broad resonance peaks to appear in the curve of resistivity versus temperature. Such

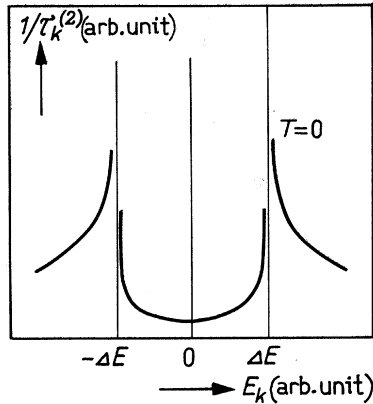


FIG. 1. The inverse relaxation time versus electron energy E_k at $T=0$. The half bandwidth $E_1=10\,000^\circ\text{K}$.

a broad peak has indeed been observed in CeAl_3 with its top at about 35°K , while the resistivity rapidly decreases towards very low temperatures.

The calculation of the resistivity as a function of temperature requires two time-consuming integrations that are currently being performed numerically. Figure 2 shows a preliminary plot of the resistivity obtained as follows: Only one side band at ΔE is assumed; the sum over k'' , whose execution led to (6) (at $T=0$), has been approximated by a function $g(E_k)$ imitating the smoothed-out logarithm that results when the sum over k'' is performed exactly at finite temperatures. The integral over the energy of this function $g(E_k)$ times the derivative of the Fermi distribution appears in Fig. 2:

$$\rho(T) \simeq \int dE_k \int dE_{k''} \left(\frac{1}{\Delta E + E_k - E_{k''}} \right) \times f^0(E_{k''}) \frac{df^0(E_k)}{dE_k}. \quad (10)$$

The results, to be published soon, can be expected to differ only quantitatively from the be-

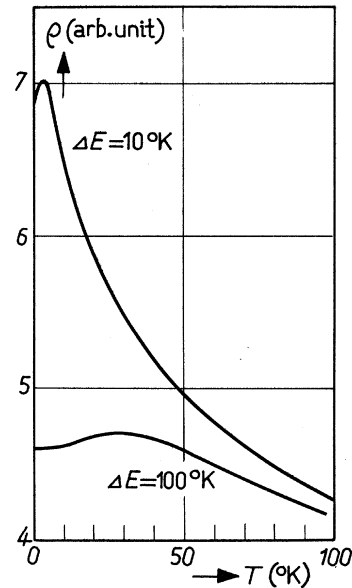


FIG. 2. The resistivity versus temperature curve for crystal-field splittings $\Delta E=10$ and 100°K . The half bandwidth $E_1=10\,000^\circ\text{K}$.

havior portrayed in the figure.

The author is grateful to Professor D. Polder, Dr. K. H. J. Buschow, Dr. H. J. van Daal, and Dr. P. Bianchessi for their stimulating criticism.

¹K. H. J. Buschow and H. J. van Daal, *Phys. Rev. Lett.* **23**, 408 (1969).

²H. J. van Daal and K. H. J. Buschow, *Phys. Lett.* **31A**, 103 (1970).

³K. H. J. Buschow and H. J. van Daal, *Solid State Commun.* **8**, 363 (1970).

⁴F. E. Maranzana, to be published.

⁵K. H. J. Buschow, to be published.

⁶J. Kondo, *Progr. Theor. Phys.* **32**, 37 (1964).

⁷T. van Peski-Tinbergen and A. J. Dekker, *Physica* **29**, 917 (1963).