SOVIET PHYSICS JETP VOLUME 26, NUMBER 4 APRIL, 1968

THE EFFECT OF MAGNETIZED LOCALIZED STATES ON THE MAGNETIC SUSCEPTIBILITY OF A SOLID SOLUTION

I. G. RATISHVILI

Physics Institute, Academy of Sciences, Georgian S.S.R.

Submitted April 9, 1967

Zh. Eksp. Teor. Fiz. 53, 1353–1361 (October, 1967)

Solutions of transition metals in which impurity ions form magnetized localized states are investigated. The localized states are described within the framework of the Wolff model but account is taken of the degeneracy of the band and of the interaction between the collectivized electrons.

INTRODUCTION

It is well known that in a series of solutions of paramagnetic ions in nonmagnetic metals the magnetic properties of the impurity centers are determined by the magnetization of the localized impurity states. Such are, for example, solutions of 3d ions in 4d metals.[1]

One of the models of the magnetized localized state was formulated in Wolff's paper.[2] Briefly it can be described in the following way.

A system of collectivized electrons described by a set of Bloch functions $\Psi_{\mathbf{k}}^{0}(\mathbf{r})$—eigenfunctions of the Hamiltonian $\mathscr{H}^0$—is perturbed by the impurity ion which has penetrated into the matrix. It is assumed that because of the difference in the Coulomb charges of the impurity ions and the matrix, and the interaction between the electrons scattered by the impurity there appears a spin-dependent potential V^{σ} which perturbs in a different way electron states with spin "up" and "down." Therefore the eigenfunctions of the perturbed Hamiltonian $\Psi_{\mathbf{k}\sigma}(\mathbf{r})$ turn out to be different for different orientations of the electron spin, $\Psi_{\mathbf{k}\uparrow}(\mathbf{r}) \neq \Psi_{\mathbf{k}\downarrow}(\mathbf{r})$. If the scattering by the impurity potential is of a resonance nature and the perturbation is concentrated in a sufficiently narrow energy interval, then one can speak of the appearance of virtual impurity states split according to the spin—localized states—with Δn^1 and Δn^2 electrons respectively. (The subscript 1 denotes the lower energy state.) It can occur that the localized state turns out to be magnetized, i.e., it turns out that $\Delta n^1 \neq \Delta n^2$; there will then appear in the space around the impurity an excess of electrons with a given spin orientation, and a so-called localized magnetic moment will appear on the impurity ion

$$\mu = {}^1\!/\!_2 g\mu_B(\Delta n^1 - \Delta n^2)$$

(g is the spectroscopic splitting factor, and μ_B is the Bohr magneton).

The described model is based on a number of approximations. It is assumed that all electrons outside the closed ion shells are collectivized, that they are in a nondegenerate band, and that the perturbation potential is concentrated at the impurity site. In this paper there are two departures from the indicated scheme: account is taken, first, of the band degeneracy, and second, of the interaction between the collectivized electrons.

The presence of localized magnetic moments is manifested at small concentrations of the solutions[1] when one can neglect the direct interaction between impurity centers. The lack of correlation in the occupation of virtual states in various impurity centers and the absence of a preferred direction lead to the circumstance that various orientations of the localized magnetic moment become equally probable.

Switching on an external magnetic field H produces a preferred direction, and the average magnetic moment of the impurity center $\langle \mu \rangle$ becomes different from zero. It results in the appearance of an additional contribution to the magnetic susceptibility of the solution which can be defined as

$$\chi_{\text{imp}} = \lim_{H\to 0} \frac{N_0\langle\mu\rangle}{H}, \tag{1}$$

if account is taken of the additivity of the contributions from different centers (N_0 is the number of impurity sites per unit volume).

The purpose of our work is the investigation of the impurity part of the susceptibility of solutions when the magnetized localized states appear in a system of interacting collectivized electrons in a degenerate band.

DETERMINATION OF THE AVERAGE VALUE OF THE LOCALIZED MAGNETIC MOMENT

Let us first consider the case of a nondegenerate band. The Hamiltonian of a perturbed crystal in the representation of second quantization of the system of unperturbed functions in site space is written in the form

$$\mathscr{H}^0 + V^\sigma = \sum_{jj'\sigma} E^0(\mathbf{r}_j - \mathbf{r}_{j'})\, a_{j'\sigma}{}^+ a_{j\sigma} + V_{00}{}^\sigma a_{0\sigma}{}^+ a_{0\sigma}, \tag{2}$$

where V_{00}^{σ} is the matrix element of the perturbation potential

$$E^0(\mathbf{r}_j - \mathbf{r}_{j'}) = \frac{1}{N}\sum_{\mathbf{k}} E_{\mathbf{k}}{}^0 e^{-i\mathbf{k}(\mathbf{r}_j - \mathbf{r}_{j'})},$$

$a_{j\sigma}^{+}$ and $a_{j\sigma}$ are the creation and annihilation operators of a state described by a Wannier function of the j-th site $w(\mathbf{r} - \mathbf{r}_j)$ which is related to the "unperturbed" and "perturbed Bloch" functions:

$$w(\mathbf{r} - \mathbf{r}_j) = \frac{1}{\sqrt{N}}\sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{r}_j}\Psi_{\mathbf{k}}{}^0(\mathbf{r}), \tag{3}$$

$$w(\mathbf{r} - \mathbf{r}_j) = \frac{1}{\sqrt{N}}\sum_{\mathbf{k}} \bar{u}_{\mathbf{k}\sigma}(\mathbf{r}_j)\Psi_{\mathbf{k}\sigma}(\mathbf{r}), \tag{3'}$$

and N is the total number of sites.

The same Hamiltonian is diagonal in momentum space in the representation of perturbed $\Psi_{\mathbf{k}\sigma}(\mathbf{r})$ functions:

$$\mathscr{H} = \sum_{\mathbf{k}\sigma} E_{\mathbf{k}\sigma} b_{\mathbf{k}\sigma}^{+} b_{\mathbf{k}\sigma}. \qquad (2')$$

Here $b_{\mathbf{k}\sigma}^{+}$ and $b_{\mathbf{k}\sigma}$ are creation and annihilation operators of "perturbed Bloch" states. They are related to the operators $a_{j\sigma}^{+}$ and $a_{j\sigma}$ according to formula (3′) by the equation

$$b_{\mathbf{k}\sigma} = \frac{1}{\sqrt{N}} \sum_{j} \bar{u}_{\mathbf{k}\sigma}(\mathbf{r}_j) a_{j\sigma}. \qquad (4)$$

Taking into account this relation, the Hamiltonian can be represented in the following form:

$$\mathscr{H} = \sum_{j'j\sigma} a_{j'\sigma}^{+} a_{j\sigma} \int E g_{j'j}^{\sigma}(E)\, dE, \qquad (5)$$

where

$$g_{j'j}^{\sigma}(E) = \frac{1}{N} \sum_{\mathbf{k}} u_{\mathbf{k}\sigma}(\mathbf{r}_{j'}) \bar{u}_{\mathbf{k}\sigma}(\mathbf{r}_j)\, \delta(E - E_{\mathbf{k}\sigma}) \qquad (6)$$

is the so-called "normalized density-of-states function."[3] It can be shown that the function $g_{j'j}^{\sigma}(E)$ can be represented in the form of a sum of two terms $g_{j'j}^{\sigma}(E) = g_{j'j}^{0}(E) + \Delta g_{j'j}^{\sigma}(E)$, the first term describing the unperturbed matrix and the second term being connected with the energy distribution of electrons in localized states. This connection is expressed in the following form[4]:

$$\Delta n^{f} = \int_{-\infty}^{\epsilon_F} \sum_{j} \Delta g_{jj}^{f}(E)\, dE. \qquad (7)$$

Here ϵ_F is the Fermi level and the superscript f = 1, 2 enumerates the localized states of an individual impurity center.

As a result of breaking up the function g(E) the unperturbed and impurity parts are also separated in the Hamiltonian (5).

The unperturbed part can be reduced to diagonal form

$$\mathscr{H}^{0} = \sum_{\mathbf{k}\sigma} E_{\mathbf{k}}^{0} a_{\mathbf{k}\sigma}^{+} a_{\mathbf{k}\sigma} \qquad (8)$$

($a_{\mathbf{k}\sigma}^{+}$ and $a_{\mathbf{k}\sigma}$ are creation and annihilation operators of Bloch states). As regards the impurity part, it must be somewhat transformed.

The perturbation produced by the impurity ion extends to the surrounding nonimpurity sites.[4] In other words, the "localized" magnetic moment turns out in essence to be smeared out in the space around the impurity. Nevertheless, in a series of experiments the total moment of an individual magnetized region manifests itself as a single entity. This means that the occupation number operators of individual sites, $n_{j\sigma} = a_{j\sigma}^{+} a_{j\sigma}$, for localized electrons are not independent. Therefore, if we take into account as a first approximation only diagonal elements of the functions $\Delta g^{f}(E)$ and introduce "the mean energy of electrons in the f-th virtual impurity state"

$$E^{f} = \int^{\epsilon_F} E \sum_{j} \Delta g_{jj}^{f}(E)\, dE \Big/ \int^{\epsilon_F} \sum_{j} \Delta g_{jj}^{f}(E)\, dE, \qquad (9)$$

then the impurity part of the Hamiltonian can be written in the form

$$\sum_{f\sigma} \Delta n^{f} E^{f} n^{f\sigma} \delta_{\sigma f},$$

where $n^{f\sigma}$ is the operator of the number of particles with spin σ in the f-th state which has eigenvalues 1 and 0, and the symbol $\delta_{\sigma f}$ is 1 or 0 depending on whether or not an electron with spin σ occupies the f-th virtual state.

It should be noted that the mean energy of the electrons localized in the f-th state can only be identified with the energy of the virtual level when these electrons are localized within a narrow energy interval.

Let us now take into account the band degeneracy. In real solutions of 3d ions in 4d metals the band in which localized states appear is doubly degenerate.[1]. In this case the magnetic moment of the impurity ion is determined by the occupation numbers of four virtual states: Δn_1^1 and Δn_1^2 in the first band, and Δn_2^1 and Δn_2^2 in the second band. Each occupation number can be expressed in terms of a Green's function of a perturbed crystal in which the two-band nature of the matrix is taken into account. The matrix elements of the Green's function and of the perturbation potential were analyzed in[5]. It turned out that the localized magnetic moments produced by one impurity ion in adjacent bands can be of different magnitude, and their orientations are in essence independent of each other. Bearing in mind the above results, the impurity part of the Hamiltonian in the degenerate case can be represented in the form

$$\sum_{n,f,\sigma} \Delta n_n^{f} E_n^{f} n_n^{f\sigma} \delta_{\sigma f}.$$

So far we have considered a system with one impurity site. If N_0 impurity ions have penetrated into the matrix and in such a way that their "spheres of influence" do not overlap (i.e., $N_0 \ll N$), then the impurity part of the Hamiltonian will be written in the form of a sum over impurity sites.

Switching on the external magnetic field leads to additional splitting of the localized states. A system of four states is formed in each band; these are occupied in pairs—either the first and the fourth or the second and the third (see Fig. 1). Taking into account this correlation, the impurity part of the Hamiltonian of the system in the external magnetic field can be represented in the following form:

$$\begin{aligned}\mathscr{H}^{\text{imp}} = \sum_{\nu=1}^{N_0} \sum_{n} \Big\{ \sum_{f} \Delta n_n^{f} \big[E_n \,(n_n^{f\uparrow}(\nu) + n_n^{f\downarrow}(\nu)) \\ - \mu_B H\, (n_n^{f\uparrow}(\nu) - n_n^{f\downarrow}(\nu))\big] \\ \times \delta(\tilde{n}_n^{1\uparrow}(\nu) + \tilde{n}_n^{1\downarrow}(\nu), 1)\, \delta(\tilde{n}_n^{2\uparrow}(\nu) + \tilde{n}_n^{2\downarrow}(\nu), 1) \\ \times [\delta(\tilde{n}_n^{1\uparrow}(\nu) + \tilde{n}_n^{2\downarrow}(\nu), 2) + \delta(\tilde{n}_n^{2\uparrow}(\nu) + \tilde{n}_n^{1\downarrow}(\nu), 2)] \Big\}. \qquad (10)\end{aligned}$$

Here $\tilde{n}$ denotes the eigenvalue of the operator n.

This form of notation allows one to determine readily the average occupancy of the virtual states in some impurity center:

$$\bar{n}_n^{f\sigma}(\nu_0) = \frac{\mathrm{Sp}\,(n_n^{f\sigma}(\nu_0)\, e^{-\mathscr{H}^{\text{imp}}\, k_B T})}{\mathrm{Sp}\,(e^{-\mathscr{H}^{\text{imp}}/k_B T})}. \qquad (11)$$

We represent the average value of the localized magnetic moment in the form

$$\langle \mu \rangle = \frac{1}{2} g \mu_B \sum_{n,f} \Delta n_n^{f} (\bar{n}_n^{f\uparrow} - \bar{n}_n^{f\downarrow}). \qquad (12)$$

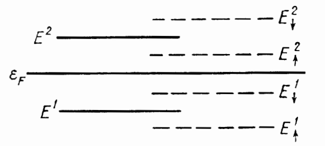


FIG. 1. Schematic diagram of the location of localized states in a nondegenerate band in an external magnetic field.

After substitution of the average occupation numbers calculated according to (11), this expression takes on the following form:

$$\langle\mu\rangle=\sum_n \mu_n \operatorname{th}\left(\frac{\mu_n H}{k_B T}\right). \tag{12'}$$

It should be noted that in deriving this dependence no explicit use has been made of the assumption that the localized states are narrow, an assumption which has for convenience been mentioned in the Introduction. An essential condition for the manifestation of the localized magnetic moment is the inequality $\Delta n^1 \neq \Delta n^2$.

ACCOUNT OF THE INTERACTION BETWEEN THE COLLECTIVIZED ELECTRONS

We shall represent the Hamiltonian of the collectivized electrons in the matrix in the form of a sum

$$\mathscr{H}_{\text{tot}}=\mathscr{H}^0+\mathscr{V}^\sigma+\mathscr{H}_c, \tag{13}$$

where $\mathscr{H}^0$ is the Hamiltonian of the non-interacting collectivized electrons in an impurity-free crystal

$$\mathscr{V}^\sigma=\sum_{\nu=1}^{N_0} V^\sigma(\nu),$$

and $\mathscr{H}_C$ is the interelectron interaction in the perturbed crystal.

In the representation of second quantization over perturbed Bloch states $\mathscr{H}_C$ is written in the form

$$\mathscr{H}_c=\sum_{mn}\sum_{\sigma\sigma'}\sum_{\mathbf{k}\mathbf{k}_1\mathbf{k}_2} b^+_{\mathbf{k}_1+\mathbf{k}m\sigma} b^+_{\mathbf{k}_2 n\sigma'} b_{\mathbf{k}_2+\mathbf{k}n\sigma'} b_{\mathbf{k}_1 m\sigma} (\mathscr{H}_c)^{\sigma\sigma'}_{\mathbf{k}_1\mathbf{k}_2\mathbf{k},mn} \tag{14}$$

$$(\mathscr{H}_c)^{\sigma\sigma'}_{\mathbf{k}_1\mathbf{k}_2\mathbf{k},mn}=\left(\Psi^m_{\mathbf{k}_1+\mathbf{k}\sigma}(\mathbf{r}_1)\Psi^n_{\mathbf{k}_2\sigma'}(\mathbf{r}_2)\left|\frac{e^2}{r_{12}}\right|\Psi^m_{\mathbf{k}_1\sigma}(\mathbf{r}_1)\Psi^n_{\mathbf{k}_2+\mathbf{k}\sigma'}(\mathbf{r}_2)\right)$$
$$-\delta_{\sigma\sigma'}\delta_{mn}\left(\Psi^n_{\mathbf{k}_1+\mathbf{k}\sigma}(\mathbf{r}_1)\Psi^n_{\mathbf{k}_2\sigma}(\mathbf{r}_2)\left|\frac{e^2}{r_{12}}\right|\Psi^n_{\mathbf{k}_1\sigma}(\mathbf{r}_2)\Psi^n_{\mathbf{k}_2+\mathbf{k}\sigma}(\mathbf{r}_1)\right). \tag{14'}$$

(Here account has been taken of the band degeneracy; m and n are band indices.)

As a first approximation we consider the averaged field produced by the collectivized electrons. To this end it is sufficient to take into account the matrix elements $\mathscr{H}_C$ corresponding to k = 0 and to confine oneself in the following to the linear approximation in the occupation number operators.

We transform expression (14) in the same way as the Hamiltonian of the perturbed crystal (2′). To this end we go over to the representation in site space, make use of the definition of the "normalized density-of-states function" (6), separate in the latter the part corresponding to the perturbation, and take into account the elements diagonal in j. As a result of these transformations we obtain

$$\mathscr{H}_c=\frac{1}{N}U\sum_{mn}\sum_{c\sigma'}(1-\delta_{\sigma\sigma'}\delta_{mn})\left[\sum_j n_m{}^\sigma(j)\right. \tag{15}$$
$$\left.+\sum_{\nu=1}^{N_0}\sum_f n_m^{f\sigma}(\nu)\Delta n_m{}^f\delta_{\sigma f}\right]\left[\sum_i n_n{}^{\sigma'}(i)+\sum_{\nu=1}^{N_0}\sum_f n_n{}^{f\sigma}(\nu)\Delta n_n{}^f\delta_{\sigma f}\right].$$

Here U is the interelectron interaction constant

$$U\approx\left(w_m(\mathbf{r}_1-\mathbf{r}_j)w_n(\mathbf{r}_2-\mathbf{r}_j)\left|\frac{e^2}{r_{12}}\right|w_n(\mathbf{r}_2-\mathbf{r}_j)w_m(\mathbf{r}_1-\mathbf{r}_j)\right).$$

Introducing the notation

$$B_m{}^\sigma=U\left[\bar{n}_m{}^\sigma+c\sum_f\Delta n_m{}^f\bar{n}_m{}^{f\sigma}\delta_{\sigma f}\right],\quad \mathscr{B}_n{}^\sigma=\sum_{m\sigma'}B_m{}^{\sigma'}-B_n{}^\sigma,\quad c=N_0/N, \tag{16}$$

the equality (15) can be written in the above approximation as

$$\mathscr{H}_c=\sum_{n\sigma}\mathscr{B}_n{}^\sigma\left[\sum_j n_n{}^\sigma(j)+\sum_{\nu=1}^{N_0}\sum_f\Delta n_n{}^f n_n{}^{f\sigma}(\nu)\delta_{\sigma f}\right] \tag{15'}$$

Substituting the latter expression in the formula for the total Hamiltonian, and separating in it the unperturbed and impurity parts, we obtain

$$\mathscr{H}_{\text{tot}}=\mathscr{H}^0{}_{\text{tot}}+\mathscr{H}_{\text{tot}}{}^{\text{imp}}, \tag{13'}$$

$$\mathscr{H}^0_{\text{tot}}=\sum_{nk}[(E_{kn}+\mathscr{B}_n)\sum_\sigma n^\sigma_{kn}-(\mu_B H+\Delta\mathscr{B}_n)(n^\uparrow_{kn}-n^\downarrow_{kn})], \tag{8'}$$

$$\begin{aligned}\mathscr{H}^{\text{imp}}_{\text{tot}}=\sum_{\nu=1}^{N_0}\sum_n\Big\{\sum_f\Delta n_n{}^f&[(E_n{}^f+\mathscr{B}_n)(n_n^{f\uparrow}(\nu)+n_n^{f\downarrow}(\nu))\\&-(\mu_B H+\Delta\mathscr{B}_n)(n_n^{f\uparrow}(\nu)-n_n^{f\downarrow}(\nu))]\\&\times\delta(\tilde{n}_n^{1\uparrow}(\nu)+\tilde{n}_n^{1\downarrow}(\nu),1)\,\delta(\tilde{n}_n^{2\uparrow}(\nu)+\tilde{n}_n^{2\downarrow}(\nu),1)\\&\times[\delta(\tilde{n}_n^{1\uparrow}(\nu)+\tilde{n}_n^{2\downarrow}(\nu),2)+\delta(\tilde{n}_n^{2\uparrow}(\nu)+\tilde{n}_n^{1\downarrow}(\nu),2)]\Big\},\end{aligned} \tag{10'}$$

where

$$\mathscr{B}_n={}^1/{}_2(\mathscr{B}_n{}^\uparrow+\mathscr{B}_n{}^\downarrow),\ \Delta\mathscr{B}_n={}^1/{}_2(\mathscr{B}_n{}^\downarrow-\mathscr{B}_n{}^\uparrow).$$

We define the magnetization of each site of the perturbed matrix in the form

$$\Delta m=m-m_0+c\langle\mu\rangle, \tag{17}$$

where m_0 and m is the magnetization due to the collectivized electrons of an individual site in the matrix devoid of impurities and in the perturbed matrix. Since the collectivized electrons obey the Pauli principle, their average magnetization is determined from the well-known equation

$$m=\mu_B\sum_n\eta_n(\varepsilon_F)[\mu_B H+\Delta\mathscr{B}_n], \tag{18}$$

in which we have in addition taken into account the band degeneracy and the interelectron interaction. Here $\Sigma_n\eta_n(\epsilon)=\eta(\epsilon)$ is the density of states per atom in a crystal without impurities.

After substituting $\Delta\mathscr{B}_n$, m takes on the form

$$m=m_0+c(q-1)\sum_n\langle\mu_n\rangle, \tag{18'}$$

where $m_0=\mu_B^2 H\eta(\epsilon_F)q$. (In the latter expressions we have used the notation $q=[1+{}^1/{}_2U\eta_n(\epsilon_F)]^{-1}$.) Now we can write the additional magnetization (17) recalculated per impurity atom in the form

$$\Delta m_{\text{imp}}=\sum_n\langle\tilde{\mu}_n\rangle\equiv\langle\tilde{\mu}\rangle, \tag{17'}$$

where $\tilde{\mu}_n=q\mu_n$. It should be noted that in experimental investigations it is precisely $\tilde{\mu}$ which is determined as the localized moment of the impurity center.

The average value of the total localized magnetic moment is calculated in accordance with the previously indicated scheme. Utilizing the expression for the impurity part of the Hamiltonian, we obtain the following formula:

$$\langle\tilde{\mu}\rangle=\sum_n\tilde{\mu}_n\operatorname{th}\left[\frac{\tilde{\mu}_n\left(H+\frac{1}{2}cU\langle\mu_n\rangle/\mu_B{}^2\right)}{k_B T}\right]. \tag{19}$$

In conjunction with (1), the obtained dependence makes it possible to determine the impurity part of the magnetic susceptibility in the high-temperature region. It turns out that χ_{imp} can be written in the form

$$\chi_{\text{imp}}(T) = \sum_n \frac{(\tilde{\mu}_n)^2}{k_B(T - T_C(n))}, \tag{20}$$

where

$$T_C(n) = c\frac{U}{2k_B}\left(\frac{\mu_n{}^2 q}{\mu_B{}^2}\right) \tag{21}$$

fulfills the role of the "Curie temperature of the n-th band."

DISCUSSION OF THE RESULTS

Let us first analyze expression (19) for the average magnetic moment. It is well known that under the condition of complete concentration of the perturbation potential at the impurity site $\Delta n_n^f \leq 1$.[4] Therefore $\mu_n \leq \mu_B$. But inasmuch as $q > 1$, $\tilde{\mu}_n$ and all the more $\tilde{\mu}$ can become larger than unity. If the spin of the impurity state is defined as $S = \tilde{\mu}/g\mu_B$, then it can correspondingly turn out to be larger than ½. Nonetheless, according to (19) the temperature dependence of the average magnetic moment is described not by a Brillouin function of the spin S (which is characteristic for a purely paramagnetic ion) but by a sum of tanh (x) functions, i.e., by a sum of Brillouin functions of spin ½. This differentiates between solutions in which a paramagnetic impurity ion produces the magnetized localized state and solutions where it retains its atomic paramagnetic properties.

On the other hand, it follows from the expression under consideration that the magnetic moment of the impurity center can be interpreted as the moment corresponding to spin ½ with an effective g factor $g_{\text{eff}} = gq(\Delta n^1 - \Delta n^2)$ only in the case of a nondegenerate band. As regards the susceptibility, under the condition that the localized magnetic moments in adjoining bands are equal, expression (20) coincides in outward appearance with the empirical dependence.[1] The difference consists in the interrelationship of the effective moment with the localized magnetic moment in the one instance, and with the spin of the paramagnetic ion in the other. (The problem has been considered in more detail in [6].) In addition to the high-temperature contribution to the susceptibility of the solution, one can compare with the experimental data the variation of the average magnetic moment in the entire temperature range and the dependence of the localized magnetic moment on the composition of the solvent alloy.

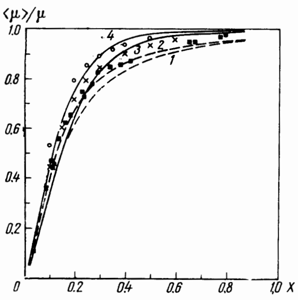


FIG. 2. Dependence of the average magnetic moment on the external field and on the temperature, $x = \mu_B H/kT$. Black squares – measurement results.[8] Dashed curves – Brillouin functions of spin S = 5 (curve 1) and S = 6 (curve 2). Solid curves – the dependence described by formula (19) for $\mu_1 = \mu_2 = 4\mu_B$ (curve 3), and $\mu_1 = \mu_2 = 5\mu_B$ (curve 4). The sequences of crosses and circles – the same dependence for $\mu_1 = 2.5\mu_B$ and $\mu_2 = 7.5\mu_B$ (crosses) and $\mu_1 = 2\mu_B$ and $\mu_2 = 6\mu_B$ (circles).

Let us consider iron solutions in Rh-Pd alloys, since both the solutions themselves as well as the solvents have been investigated experimentally.[1,7,8] In Fig. 2 the sequence of black squares shows the results of measurements of the average magnetic moment in a dilute PdFe solution; the average magnetic moment was determined from the variation of the hyperfine field at the impurity nucleus.[8] The theoretical results are illustrated by the curves and sequences of points. As can be seen from the comparison of the experimental and theoretical data, it is so far impossible to accord our preference to any of the forms of the temperature dependence—the Brillouin function or the dependence described by (19)—since equally satisfactory results are observed in both cases.

There are two reasons for the change in the localized moment $\tilde{\mu}_n$ on changing the composition of the solvent. First, the difference $(\Delta n^1 - \Delta n^2)$ and, secondly, q is not constant.

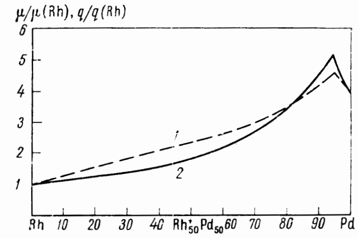
Both the electronic specific heat and the magnetic susceptibility increase in Rh-Pd alloys with increasing Pd concentration. Both quantities are proportional to the density of states at the Fermi level. But in the interval between Rh and Pd the specific heat increases by about a factor of two and the susceptibility increases almost by a factor of six.[7] This deviation may be due to the interaction between the collectivized electrons.

It has in fact turned out that in the entire interval from Rh to Pd the experimental data on the specific heat and the magnetic susceptibility agree with each other if the susceptibility per matrix site is described by the expression $\chi^0 = \lim_{H \to 0} m_0/H$ where m is given by (18″) with an interelectron interaction constant in the interval 0.6–0.9 eV. Consequently, the factor q can be estimated from the ratio of the susceptibility of the matrix to the Pauli susceptibility calculated from the measured specific heat.

Figure 3 shows the variations of the experimental values of the localized magnetic moment $\tilde{\mu}_n$[1] and the factor $q = \chi^0/\chi_{\text{Pauli}}$ determined according to the data of [7]. It can be concluded from the graph that in the solutions under consideration with the change in the solvent the variation of the difference $(\Delta n^1 - \Delta n^2)$ takes place within a limited interval. In addition, it follows from this graph that one can indeed consider the strong effective interelectron interaction in the matrix to be the reason for the appearance of anomalous magnetic moments in these solutions.

Summarizing all that has been said above, one can conclude that the production of magnetized localized states by paramagnetic ions leads to the appearance of a temperature-dependent contribution to the magnetic susceptibility of the solution. In the general case the

FIG. 3. Variations of the localized magnetic moment (curve 2) and of the coefficient q (curve 1) with changing composition of the solvent. (The curves are normalized to the corresponding values in Rh.)



temperature dependence of the impurity part of the susceptibility differs from the Brillouin function, but in the region of high temperatures it goes over into the Curie-Weiss relation. On the other hand, if the magnetized localized states are produced in a nondegenerate band, then their contribution to the susceptibility can be interpreted as a contribution from spins $\frac{1}{2}$ with some effective g factors.

The following has been explained from a comparison with experimental data. In the Fe-Pd solution the temperature dependence of the average value of the localized magnetic moment can be described by formula (19), if one allows from the double degeneracy of the band and assumes that there appears in one of the bands a localized moment of the order of $(4-7)\,\mu_B$. The anomalously large value of the moment appears admissible under the condition of the existence of a sufficiently large magnetization factor q. A comparison of the data on the magnetic susceptibility and the specific heat shows that in Rh-Pd matrices q actually reaches the required values.

---

[1] A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125**, 541 (1962).

[2] P. A. Wolff, Phys. Rev. **124**, 1030 (1961).

[3] D. A. Goodings and B. Mozer, Phys. Rev. **136**, A1093 (1964).

[4] I. G. Ratishvili, Fiz. Tverd. Tela 7, 2933 (1965) [Sov. Phys.-Solid State 7, 2381 (1965)].

[5] I. G. Ratishvili, Fiz. Metal. Metaloved., in press.

[6] I. G. Ratishvili, Tenth International Conference on Low-temperature Physics, Moscow, 1966.

[7] D. W. Budworth, F. E. Hoar, and J. Preston, Proc. Roy. Soc. **A257**, 250 (1960).

[8] T. A. Kitchens and P. P. Craig, J. Appl. Phys. **37**, 1187 (1966).

Translated by Z. Barnea
156