SPIN DENSITY FLUCTUATION SPECTRUM IN METALS WITH PARAMAGNETIC IMPURITIES

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An analysis of the fluctuation spectrum of impurity spin density in metals at \( T \ll T_K \) (Kondo temperature) is carried out. It is shown that due to inhibition of low frequency fluctuations, elastic paramagnetic scattering of neutrons by an impurity metal should be considerably weakened. The effect of bound state formation on the hyperfine structure of the Mossbauer line of impurity nuclei is also discussed.

**INTEREST** in the study of low-temperature properties of metals containing small amounts of paramagnetic impurities has greatly increased recently. Following the publication of the theoretical paper of Kondo \(^1\) who observed anomalies in the cross section of the exchange scattering of conduction electrons by localized impurity spins, it became clear that many singularities of electric, magnetic, and thermal properties of metals with d-impurities are due to the dynamic character of the s-d interaction.

Numerous experimental investigations of the properties of simple metals with small additions of transition elements indicate that when the temperature drops below a certain characteristic quantity \( T_K \) (Kondo temperature), bound states of conduction electrons with impurity spins are produced. This is one of the manifestations of the dynamic character of the antiferromagnetic exchange s-d interaction in a degenerate system of electrons. One can apparently regard it as established \(^2\) that when the temperature is lowered (in the region \( T < T_K \)) the local spin moment of the impurity is gradually compensated by the "cloud" of conduction electrons, so that at \( T = 0 \) we arrive at a fully spin-compensated ground state of the impurity system. This is indicated both by macroscopic measurements (susceptibility) and by microscopic data (NMR, Mossbauer effect).

Following the formation of bound states, the frequency spectrum of the spin-density fluctuations of the impurity regions is noticeably changed. As will be made clear subsequently, when \( T < T_K \) the low frequencies \((\omega \ll T_K)\) turn out to be strongly suppressed and the main part of the spectral density is concentrated in the region of frequencies of the order of the binding energy of the electron-impurity pairs.

In connection with the foregoing, particular interest attaches to experiments which make it possible to investigate directly the spatial distribution and the dynamics of the spin density of the impurity regions in metals at \( T < T_K \). As is well known, such information can be obtained in principle by investigating the angular and energy distributions of slow neutrons scattered by an impurity system. We present below a qualitative analysis of the characteristic features of the cross section of impurity paramagnetic scattering of neutrons in the region \( T < T_K \). In addition, we discuss briefly certain features of the hyperfine structure of the Mossbauer line of impurity nuclei.

Let us examine the process of scattering of a monochromatic beam of neutrons by a metal containing a small number of paramagnetic impurities, whereby neutrons with initial momentum \( p \) go over into a final state with momentum \( p' \) (the energy changes by an amount \( E_p - E_{p'} \)). The double-differential cross section of the magnetic scattering of the neutrons by the impurities system, which is in a disordered state, is given by the standard formula

\[
\frac{d\sigma}{d\Omega dE_{p'}} = \frac{2}{3} (\pi r_0)^2 \frac{1}{2} \int_{-\infty}^{\infty} \langle \hat{S}_q^2(t) \rangle \exp \{ i(E_p - E_{p'})t \} dt, \quad q = p - p',
\]

where \( \hat{S}_q \) is the Fourier component of the spin density in the sample, \( r_0 \) is the magnetic moment of the neutron (in nuclear magnetons), and \( r_q \) is the classical radius of the electron. Denoting the Fourier component of the spin density of the conduction electrons by \( S_q \), and the magnetic form factor of the impurity atom by \( F_q \), we can represent the quantity \( \hat{S}_q \) in the form

\[
\hat{S}_q = S_q + F_q \sum_i S_i \exp(-i\mathbf{q}\mathbf{R}_i),
\]

where \( \mathbf{R}_i \) is the lattice site on which the paramagnetic atom with spin \( S_i \) is localized.

In the approximation linear in the concentration, the impurity part of the magnetic-scattering cross section is written in the form

\[
\frac{d\sigma_{\text{im}}}{d\Omega dE_{p'}} = N_i \frac{2}{3} (\pi r_0)^2 \sqrt{E_{p'}} \Phi_q (E_p - E_{p'}),
\]

where the dynamic spin form factor of the impurity region is

\[
\Phi_q (\omega) = |F_q|\langle S|S \rangle_\omega + 2 \text{Re} F_q \langle S^+|S \rangle_\omega + \langle S^+|S^+ \rangle_\omega^0,
\]

and we have introduced the notation

\[
\langle A|B \rangle_\omega = \sum_{n,m} \langle A | n \rangle \langle m | B \rangle \exp\{i\omega t\} dt.
\]

In formula (1), \( N_i \) is the number of paramagnetic atoms in the sample, and the quantity \( \Phi_q (\omega) \) pertaining to one impurity (the symbol \( \langle \ldots \rangle_\omega^0 \) denotes the impurity part of the corresponding correlator).

In the zeroth approximation, when the impurity spins are assumed to be perfectly free, the function \( \Phi_q (\omega) = S(S+1) |F_q| \langle S^+ |S^+ \rangle_\omega^0 \), and we arrive at the usual expres...
sion for the cross section for elastic paramagnetic scattering of neutrons by a system of disordered localized spins:

$$\frac{d\sigma}{d\Omega dE} = \frac{N}{3} \left(\pi r_0^2\right)^{3/2} |F_3|^2 |E_p - E_f|.$$  

Allowance for the exchange s-d interaction of the impurity spins with the conduction electrons causes the spectral distribution to become deformed and, as will be shown later, it does not reduce to a simple broadening of a $\delta$-like peak (as would be the case in the region $T \gg T_K$) when the bound states are produced. The spin density of the conduction electrons turns out to be spatially correlated with the localized impurity spins, and when $T \ll T_K$ this correlation reflects the effects of low-temperature spin compensation, and does not reduce to a weak demagnetization of the s-electrons near low-temperature spin compensation, and does not resemble the region $T \approx T_K$.

In analyzing the properties of metals containing paramagnetic impurities, one frequently resorts to a simplified model with a Hamiltonian

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_{imp},$$

with $\mathcal{H}_s$ pertaining to the system of the conduction electrons, and the exchange interaction of the localized impurity spins with the conduction electrons is specified by the contact term

$$\mathcal{H}_{imp} = -J_0 \sum \mathcal{S}_0(\mathbf{r}_i),$$

where the spin density of the s-electrons is $\mathcal{S}(\mathbf{r}) = \psi^*_s(\mathbf{r}) \mathcal{S}_0(\mathbf{r}) \psi_s(\mathbf{r})$, and $\mathcal{S}_0$ is the specific volume.

We shall consider below a metal with a single magnetic impurity, localized at the site $\mathbf{R}_0 = 0$, and represent the exchange interaction, following Abrikosov\(^{[31]}\) in the form

$$\mathcal{H}_{imp} = -J_0 \sum (\mathcal{S}_0(\mathbf{r}_i) \psi^*_s(\mathbf{r}) \psi_s(\mathbf{r}),$$

where $\psi_s(\mathbf{r})$ is the operator of creation (annihilation) of an impurity pseudoparticle. Since we shall be henceforth interested in the temperature region $T \ll T_K$, we can retain in (3) only that part of the interaction which is responsible for the formation of the bound states of the conduction electrons with the impurity spin, and start from the expression

$$\mathcal{H}_{imp} = \Delta_{0} \psi^*_s \psi^* - \Delta_{0} \psi \bar{\psi} - \Delta \psi^*_s \psi^* \bar{\psi} + \Delta \psi \bar{\psi},$$

Strictly speaking, the coefficients $\Delta_{0} \psi^*_s \psi^*$ can be calculated in a self-consistent manner only in the case of an impurity with spin $S = 1$.\(^{[41]}\) However, in order to simplify the formal aspect of the problem as much as possible, we shall turn below to the case of an impurity with $S = \frac{1}{2}$, and will regard the quantities $\Delta_{0} \psi^*_s \psi^*$ as parameters of the theory, assuming that some of them differ from 0 below $T_K$. We can hope to obtain thereby qualitatively reasonable results, at least in the region $T \ll T_K$.

Assuming that singlet bound states of the conduction electrons with the impurity spin ($J < 0$) are produced when $T < T_K$, we should put

$$\Delta_{0} \psi^*_s = \lambda \langle S_0 \rangle \psi^*, \quad \Delta \psi^*_s \psi^* = \lambda \bar{\psi},$$

and the parameter $\lambda$ determines the binding energy of the electron-impurity pair. We shall assume from now on that there is no external magnetic field.

Introducing the impurity temperature Green’s function

$$G_{\beta} (\omega_n) = \langle T (\psi_n (\mathbf{r}) \psi_n^*) \rangle,$$

we can readily obtain for its Fourier transform the following simple expression

$$G_{\beta} (\omega_n) = \frac{1}{\omega_n - \Delta - \text{sign} \omega_n},$$

where the binding energy is $\Delta = 2p_0J\gamma^2 \gamma_0$ ($\gamma$ is the density of the electronic states at the Fermi level).

It is also easy to show that the electronic Green’s function can be written in the following representation in the form

$$G_{\beta} (\omega_n) = \frac{1}{\omega_n - \Delta - \text{sign} \omega_n},$$

where the “scattering matrix” is

$$G_{\beta} (\omega_n) = \frac{1}{\omega_n - \Delta - \text{sign} \omega_n}.$$

As to the “anomalous” functions $F_{\beta} (\mathbf{r}, \omega_n)$, which are the Fourier transforms of the quantities

$$F_{\beta} (\mathbf{r}, \omega_n) = \langle T (\psi(\mathbf{r}, \omega_n)) \rangle,$$

which are analogous to the Gor’kov functions in the theory of superconductivity, they are given in the momentum representation by the formula

$$F_{\beta} (\mathbf{r}, \omega_n) = \frac{1}{\omega_n - \Delta - \text{sign} \omega_n}.$$

Using the standard technique, we can express the Fourier transforms of the correlators which enter equation (2) for the dynamic spin form factor $F_\beta (\omega_n)$ in terms of the spectral densities of the temperature Green’s functions $\Phi (\omega_n)$, $\Phi (\omega_n)$, and $G(\omega_n)$. It is easy to show, for example, that

$$\langle S \rangle = 2S(1 + Q - 2Q) \langle e^{i \omega \cdot \mathbf{Q}} \rangle \langle \psi^*_s \psi(\omega + \omega') \psi(\omega') \rangle \langle 1 - f(\omega + \omega') \rangle d\omega',$$

where $f(\omega) = e^{\omega/T + 1} - 1$, and the spectral density of the impurity pseudoparticles is

$$\Phi (\omega) = \frac{1}{\pi} \frac{\Delta}{\omega^2 + \Delta^2}.$$

The factor $Q^{-1}$ in (4) has been introduced to “compensate” for the unphysical impurity states, and it is easy to verify that in the case under consideration ($S = \frac{1}{2}$) we have

$$Q = \frac{1}{2} + \sum \rho \left[ 2T \sum \mathbf{r}_n \mathbf{r}_n^{\prime} \right]^2.$$
It is easy to construct without difficulty the quantity $\langle S | S \rangle_\omega$ at $T = 0$, when the entire spectral density of the fluctuations of the localized spin is shifted to the region of positive frequencies. A direct calculation shows that in the ground state

$$\langle S | S \rangle_\omega = \int \frac{d\omega}{\omega} \frac{\Delta^2}{\omega} \left[ \frac{1}{\Delta \omega} \ln \left( 1 + \frac{\omega^2}{\Delta^2} \right) \right],$$

with $\Delta \sim T_K$. A plot of the function $S(\omega) = \langle S | S \rangle_\omega / (6/\pi^2 \Delta^2)$ for the case $T = 0$ is shown in the figure. It is easy to verify that when $T < T_K$ we get $S(0) \approx T/2\Delta \ll 1$. We see that the low-frequency region of the spectrum turns out to be suppressed.

The dynamic spin form factor $\Phi_Q(\omega)$ of the impurity region can be reduced to a form similar to the expression for the local correlator (4):

$$\Phi_Q(\omega) = 2S(S+1)Q^{-1} \int \Gamma_Q(\omega', \omega + \omega) g(\omega') g(\omega'),$$

where the kernel $\Gamma_Q(\omega', \omega)$ has a rather complicated structure and its explicit form will not be presented here. It is easy to note, however, that we get $\Phi_Q(0) \rightarrow 0$ when $T \rightarrow 0$, i.e., the low-frequency region of the spectrum of the dynamic neutron form factor also turns out to be suppressed when $T < T_K$. This means that purely elastic paramagnetic scattering of neutrons is strongly suppressed at low temperatures. This is simply due to the fact that singlet bound states are characterized by rapid quantum fluctuations of the impurity spin density, with an average period $\sim 1/\Delta$, and in neutron scattering the most probable is the inelastic process with an energy transfer $\sim \Delta$. We note that for many impurity systems (for example Au-V) the quantity $\Delta$ is of the order of several hundred degrees.

A direct measurement of the quantity $\Phi_Q(\omega)$ at different values of the transferred momentum $q$ should be made by observing the inelastic scattering of neutrons by impurity metals; however, useful information concerning the profile of the frequency distribution of the dynamic form factor can also be obtained by measuring the impurity-scattering cross section integrated with respect to the final neutron energy, given by the expression

$$d\sigma_Q^{(0)} / d\Omega = \frac{1}{2} \langle N(\omega) \rangle^2 \gamma(\theta, E_p),$$

where

$$\gamma(\theta, E_p) = \frac{1}{2} \int \frac{E_p}{E_p} \Phi_q(E_p - E_p) dE_p = \frac{1}{2} \int \frac{1}{E_p} \Phi_q(\omega) d\omega.$$ 

Formula (5) describes the dependence of the angular distribution of the impurity part of the magnetic scattering of a monochromatic beam of neutrons on the initial energy $E_p$. When $E_p \ll \Delta$, which is perfectly feasible when $T < T_K$ (for example, for the impurity system Au-V mentioned above), $\gamma(\theta, E_p)$ should be much smaller than its traditional value $S(S+1) | F_Q |^2$. This is the result of the above discussed dynamic suppression of the impurity magnetic scattering with small energy transfer.

In the case when $E_p \gg \Delta$, we can use the static approximation, in which the angular distribution is described by the formula

$$S_{tot} = S + \int s(\tau) d\tau,$$

and in the case of total compensation of the impurity spin we have $S_{tot}^{(1)} \rightarrow 0$ as $T \rightarrow 0$. We note that, as can be readily verified, for the foregoing simple model of singlet pairing of the conduction electrons with an impurity having a spin $S = 1/2$ we get

$$S_{tot}^{(1)} = \frac{2}{\pi} \left( \frac{1}{2} + \frac{\Delta}{2\pi T} \right) S(S+1),$$

where $\Psi(x)$ is the logarithmic derivative of the $\gamma$ function. When $T \ll \Delta$ we get $S_{tot}^{(1)} \approx T/\Delta$.

The unique character of the low-temperature quantum fluctuations of the impurity electron spin, which we described above, can lead to a curious temperature dependence of the hyperfine structure of the Mossbauer spectrum of impurity nuclei. The hyperfine splitting is due to the interaction

$$\mathcal{H}_{hf} = 4IS = A(S) + AIS,$$

where $I$ is the spin of the impurity nucleus, and for a paramagnet in the absence of an external field we have $\langle S \rangle = 0$, and, as is well known, in this case the Mossbauer spectrum has a resolved hyperfine structure only if the condition $\omega_N T \gg 1$ is satisfied, where $\omega_N = A/\gamma N S$ is the frequency of the nuclear precession around the instantaneous direction of the impurity electron spin, and $\tau$ denotes the average time of reorientation of the latter. In metals, when $T > T_K$, it can be assumed that $1/\tau \approx (J_p)^{-1}$, and at a sufficiently low temperature, but still higher than $T_K$, the condition of slow electron relaxation may be attained. This is quite likely, since in the low-temperature region, owing to the "bottleneck" effect, $\tau$ is in fact much larger than the value calculated from the formula presented above. Thus, for impurity systems with a sufficiently low value of $T_K$ it may happen that already when $T > T_K$ the hyperfine structure of the Mossbauer spectrum of the impurity nuclei is already distinctly formed, but with further lowering of the temperature, instead of being stabilized, it should be destroyed by the onset of fast fluctuations of the impurity electron spin, accompanying the formation of the bound states. The picture described above can take place for spectra of Fe$^{57}$ nuclei in the Cu-Fe impurity system, where $T_K \approx 15^\circ K$.

We note in conclusion that the realignment of the spectrum of the impurity-spin fluctuations should influence the character of the low-temperature spin-lattice relaxation of the impurity nuclei. This question was recently discussed by the authors of the present paper.[7]