Temperature variations in induced hyperfine field and the Fermi energy in magnetically ordered 3*d*- and 4*f*-metals

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It is shown that the so-called temperature anomalies of the hyperfine field at nuclei of a nonmagnetic impurity in 3*d*- and 4*f*-metals are a natural consequence of the complex nature of the curves representing the local density of states of the impurity electrons. As an example, the experimental data for the iron matrix and the rare-earth matrix are considered; they show that with increasing temperature the deviation of the hyperfine field $\Delta H(T)$ from the spontaneous magnetization curve $M(T)/M(0)$ increases approximately linearly with decreasing magnetization. In a number of cases, however, there is a deviation from linear dependence. Such behavior can be attributed to the variation of the local density of states of electrons with opposite spins near the Fermi energy.

1. INTRODUCTION

Data presently exist for hyperfine (HF) fields at nuclei ($H_{\rm HF}$) for most of the atoms of the periodic table introduced as substitutional impurities in iron, cobalt and nickel matrices. In rare-earth matrices, $H_{\rm HF}$ is measured only for 5*sp*- and 5*d*-impurities in gadolinium and for a few impurities in other rare-earths and intermetallic compounds. Theoretical calculations of these so-called induced HF-fields have been carried out *ab initio*[1,2] based on the theory of Teracura[3] for all impurities from $Z = 1$ to $Z = 56$ in iron and nickel matrices. The results give excellent agreement with the observed dependence of $H_{\rm HF}$ on Z; from this it follows that the formation mechanism of the HF-field in a 3*d*-metal is primarily connected with the properties of the hybridized metal *d*-band (see for example Ref. 4).

However, the experimentally observed temperature dependence of $H_{\rm HF}(T)$ for a nonmagnetic impurity, as a rule, deviates from the spontaneous magnetization curve $M(T)$ of the matrix. These deviations, sometimes referred to as HF-field temperature anomalies, have not at present been explained.

This article is concerned with the interpretation of these temperature effects based on the band model, taking into account that the local density of states for impurities and matrices usually have a complex structure, characterized by sharp peaks and sudden dips.

2. DEPENDENCE OF THE TEMPERATURE ANOMALY ON MAGNETIZATION

For nonmagnetic impurities of the *sp*-elements the principal contribution to the HF-field is given by the Fermi interaction

$$H_{\rm HF}=\frac{8\pi}{3}\mu_B\int^{E_F}[\rho_s{}^{\uparrow}(0,E)-\rho_s{}^{\downarrow}(0,E)]\,dE, \tag{1}$$

where μ_B is the Bohr magneton, E_F is the Fermi energy, and $\rho_s^\sigma(0,E)$ is the local density of states at the impurity center for electrons with energy E and spin σ ($\sigma = \uparrow$ or $\downarrow$). These are taken to have *s*-symmetry about the impurity center. The local density of states $\rho_s^\sigma(0,E)$ is determined by the square of the wave function at the impurity center $\psi_s^\sigma(0,E)$ normalized within the impurity MT-sphere of radius r_i, and by the density of states with a given energy, $\rho_s^\sigma(E)$:

$$\rho_s{}^\sigma(0,E)=\frac{1}{4\pi}\{\psi_s{}^\sigma(0,E)\}^2\rho_s{}^\sigma(E). \tag{2}$$

These *s*-symmetry states consequently hybridize, the *s*-states at the center mixing with the resonant *d*-orbitals of the surroundings directed at the center. The contribution from core polarization turns out to be small for the impurities investigated, and is not considered. The local state densities $\rho_s^\sigma(0,E)$ and the integral state densities $\rho_s^\sigma(E)$ for each spin direction in the impurity sphere are calculated in Refs. 1 and 2 for temperature $T = 0$ K. They are not uniform functions of energy, but have a significant structure and differ substantially for states in opposite spin directions.

To find theoretically the HF field for a temperature $T > 0$ K leading to a constant volume, it is necessary to carry out calculations of the local density of states at this temperature. This is an unsolved problem at present. However, it is possible to determine the change in $H_{\rm HF}(T)$ for a temperature change from T_0 to T, without recourse to complex calculations, starting from the following simple considerations. In the ferromagnetic state the energies E' and E'' of electrons of opposing spins differ by the exchange splitting Δ:

$$E'=E^{\uparrow}+\Delta,\quad E''=E^{\downarrow}-\Delta, \tag{3}$$

where E^σ is the electron energy without account of the exchange interaction; i.e., the energy in the paramagnetic state. In the usual version of the Stoner model we have $\Delta = -IM(0)$, where I is the exchange splitting constant and $M(0)$ is the magnetization at $T = 0$ K. In the spin-density functional formalism the exchange splitting depends on energy. Results found in Ref. 5 show that $I(E)$ can be approximated as a linear function of energy. For the 3*d*-transition metals in the right half of the period, $I(E)$ is larger near the top of the band than at the bottom:

$$\Delta(E)=-(I+kE)M(0), \tag{4}$$

where I and k are constants. If we assume that Eq. (4) remains valid at a temperature T for the mean value $M = \langle M\rangle_T$, the expression for $H_{\rm HF}(T)$ can be written as a difference between integrals over the two sub-bands:

$$H_{\rm HF}(T)=\int^{\xi}\rho^{\uparrow}(0,E^{\uparrow}+\Delta)\,dE'-\int^{\xi}\rho^{\downarrow}(0,E^{\downarrow}-\Delta)\,dE''. \tag{5}$$

Here we have set the constant coefficient $(8\pi/3)\mu_B$ to unity

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and dropped the index s. The chemical potential ξ, in the magnetically ordered regime at temperatures low compared to the Fermi temperature, is practically identical with the Fermi energy E_F. It is, however, easy to see that if the densities of states $\rho\uparrow(E_F)$ and $\rho\downarrow(E_F)$ at the Fermi level differ, then the chemical potential will change as a function of temperature, not because of the temperature broadening of the Fermi edge, but due to the variation in the magnetization $M(T)$. To determine the variation of $H_{\mathrm{HF}}(T)$ caused by the magnetization decrease $\Delta M = M(T) - M(T_0)$, we can expand the functions to be integrated in Eq. (5) in powers of ΔM, and terminate the expansion at the linear term, or take the derivative with respect to M of the expression under the integral sign. Then we get

$$H_{\mathrm{HF}}(T)=H_{\mathrm{HF}}(T_0)+\{\rho(0,\xi)-\alpha[\rho^{\uparrow}(0,\xi)-\rho^{\downarrow}(0,\xi)]\}I\Delta M$$
$$+k\Delta M[E_m{}^{\uparrow}\rho^{\uparrow}(0,\xi)+E_m{}^{\downarrow}\rho^{\downarrow}(0,\xi)], \tag{6}$$

where

$$\alpha=\frac{d\xi}{dM},\qquad E_m{}^{\uparrow}=\frac{\xi-IM}{1+kM},\qquad E_m{}^{\downarrow}=\frac{\xi+IM}{1-kM}.$$

The quantity α is determined from the condition that the total electron number does not change when electrons pass from one sub-band to another, i.e.,

$$\frac{d}{dM}\left[\int^{\xi}\rho^{\uparrow}(0,E^{\uparrow}+\Delta)\,dE'+\int^{\xi}\rho^{\downarrow}(0,E^{\downarrow}-\Delta)\,dE''\right]=0. \tag{7}$$

If we neglect the dependence of Δ on E, then from (7) we get

$$\frac{d\xi}{dM}=-I\frac{\rho^{\uparrow}(\xi)-\rho^{\downarrow}(\xi)}{\rho(\xi)}, \tag{8}$$

$$\xi=\xi_0-\alpha\Delta M. \tag{9}$$

Thus we see that the position of the Fermi level will change as the magnetization varies, according to the size and sign of α. It is convenient to represent the size of the temperature anomaly in $H(T)$ in terms of the deviation of the curve $H_{\mathrm{HF}}(T)$ from the spontaneous magnetization curve:

$$\Delta H(T)=H_{\mathrm{HF}}(T)-H_{\mathrm{HF}}(T_0)\,\frac{M(T)}{M(T_0)} \tag{10}$$

From Eqs. (6) (at $k=0$), (8) and (10) it follows that

$$\Delta H(T)=H_{\mathrm{HF}}(T_0)\left\{\frac{1}{H_{\mathrm{HF}}(T_0)}IM(T_0)\cdot\right.$$
$$\left.\times\left[\rho(0,\xi)-\frac{(\rho^{\uparrow}(0,\xi)-(\rho^{\downarrow}(0,\xi))^2}{\rho(0,\xi)}\right]-1\right\}\frac{\Delta M}{M(T_0)}\cdots. \tag{11}$$

Here we have replaced the density-of-states relation introduced in Eq. (8) by the local density of states relation in accordance with Eq. (2). We see from Eq. (11) tha $\Delta H(T)$ will be non-zero if $\rho(0,\xi)$ and $\rho^{\sigma}(0,\xi)$ are not constant over the whole temperature interval from 0 K to T_c.

The expression (6), derived on the assumption that the exchange splitting depends on E, contains terms in which the quantities E_m^{σ} appear. These quantities, containing ξ, also appear in the expression for α, and lead to a quadratic ΔM-dependence.

3. ANALYSIS OF EXPERIMENTAL DATA

In Fig. 1 experimental data[6] are shown for $\Delta H(T)$ as a function of magnetization $\Delta M/M(0)$, for several impurities in ferromagnetic iron, and for atoms of the iron matrix itself. For impurities of antimony, tin, indium, copper, gold and for iron itself the deviation is positive; for arsenic impurities it is negative. The values of $\Delta H(T)$ increase smoothly with ΔM and lie along "broken" curves, or curves with small deviations from linear dependence. The positions of a few points do not lie on the corresponding curve. According to Eq. (11), a nonzero $\Delta H(T)$ value must arise as a consequence of nonconstant local densities of states $\rho(0,\xi)$ and $\rho^{\sigma}(0,\xi)$. In fact, if the local densities of states at the Fermi level change with temperature, the measured value of $H_{\mathrm{HF}}(0)$ will not be determined by the expression in curly brackets in the first term in $1/H_{\mathrm{HF}}(0)$ in Eq. (11); consequently this term will differ from unity. The local densities of states at impurity centers in iron and nickel matrices, shown in Refs. 1 and 2 and also in Ref. 7, show convincingly that for a relative band splitting upward and downward $\rho(0,\xi)$ and $\rho^{\sigma}(0,\xi)$ change sharply, as a rule. A linear variation of $\Delta H(T)$ in some interval ΔM means that in the corresponding temperature interval $\rho(0,\xi)$ and $\rho^{\sigma}(0,\xi)$ remain constant, variation in these quantities occurring only at other temperatures. Deviations of experimental points from a straight line at some temperatures signal changes in the local densities of states at the Fermi level at these temperatures. If the behavior of the experimental points in Fig. 1 is treated as a nonlinear dependence, this dependence can be connected with the presence of terms in Eq. (6) quadratic in ΔM, which were mentioned above.

The observed temperature dependence of $H_{\mathrm{HF}}(T)$ for a nonmagnetic impurity in rare-earth metals can have a behavior similar to the present case of the $3d$-matrix. Although

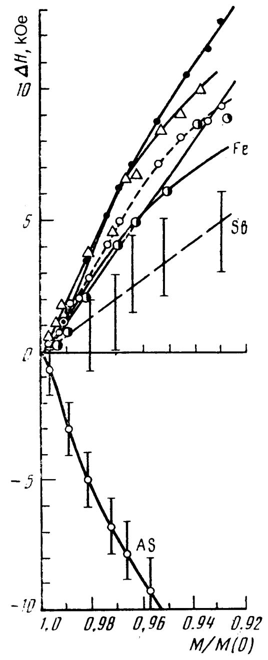

FIG. 1. Deviation ΔH in induced HF-field as a function of magnetization $M/M(0)$, for nuclei of nonmagnetic impurities and for the iron matrix itself: Δ—Au ($\Delta H/10$), ●—In, ○—Cu, ◑—Sn.

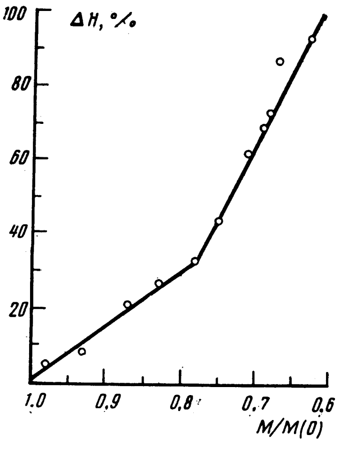

FIG. 2. Deviation of induced HF-field as a function of $M/M(0)$ for Sn in a Tb matrix. Values of ΔH given as percentages for $M/M(0)$.

calculations of the electronic structure for an impurity in the rare-earth metals have not been carried out, we may expect that the impurity densities of states are also determined by hybridization of the *d*-band states with the *sp*-states of the impurity, and have a complex structure with sharp peaks, like the density of states of the pure metal matrix, which has been calculated theoretically (see, for example, Ref. 8). The temperature dependences of the HF-fields for nonmagnetic impurities in rare-earth metals are measured only for tin and cadmium impurities in matrices of gadolinium, terbium, dysprosium and holmium.[9–13] In the case of the gadolinium matrix the anomalies are insignificant. In the remaining cases the anomalies are very large; for the helical and umbrella-shaped magnetic structures of dysprosium and holmium the HF-field deviation for tin, $\Delta H(T)$, is somewhat larger than for terbium in the region of collinear ferromagnetic structure. When correction is made for noncollinear structure, the deviations $\Delta H(T)$ in terbium, dysprosium and holmium are almost identical.

As an example, data for $H(T)$ in a terbium matrix are shown in Fig. 2. They demonstrate that the anomaly is positive, and the values of $\Delta H(T)$, as in the case of $3d$-matrices, increase almost linearly as $M/M(0)$ decreases. The slope of the line changes at $M/M(0) \sim 0.82$. This result agrees with the hypothesis that the HF-field temperature anomalies in $3d$- and $4f$ metals have the same character. In addition, it illustrates that measurements carried out in a wider temperature interval, as in the example of tin impurities in rare-earth metals, allow detection of variations in the local densities of states at the Fermi level; these appear in the variation of the original linear dependence of ΔH on ΔM. Similar changes cannot be directly demonstrated in the series of cases studied of impurities in iron, where measurements were taken over a comparatively narrow temperature (and ΔM) interval. The absence of an HF-field temperature anomaly for, for example, cadmium and tin in gadolinium means that $\rho(0,\xi)$ and $\rho^{\sigma}(0,\xi)$ are independent or weakly dependent on temperature.

4. DISCUSSION AND CONCLUSIONS

The mechanism studied for the origin of the temperature anomalies applies not only to pure matrices, but also to alloys, when the induced HF-fields are created by band electrons with a complex structure for the local densities of states at the sites.

Our basic conclusion is that temperature anomalies in the induced HF-field result from sharp peaks in the local densities of states at the sites, due to a complex impurity electronic structure. A similar character for the electronic structure of a pure matrix should lead to an analogous effect—polarization of the band electrons, given by

$$P=\int^{\xi}[\rho^{\uparrow}(E)-\rho^{\downarrow}(E)]dE\Big/\int^{\xi}[\rho^{\uparrow}(E)+\rho^{\downarrow}(E)]dE, \quad (12)$$

which does not follow from the magnetization $M/M(0)$.

Temperature variation in electronic structure in iron and nickel is being intensively studied by photoemission spectroscopy, with angle and spin resolution. These experiments show that polarization does not follow from magnetization $M/M(0)$ (see, for instance, Refs. 14 and 15), although data taken by this method relate to the surface layers of the metal studied. The same conclusion follows from the observed temperature anomaly $H_{\mathrm{HF}}(T)$ for tin impurities in rare-earth metals.[10] Sufficiently precise measurements of temperature anomalies in the induced HF-field can give essential information on the local densities of states.

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