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PRESSURE DEPENDENCE OF THE MAGNETIZATION OF IRON AT ZERO TEMPERATURE

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The connection between magnetism and chemical bonding, in particular the occurrence of atomic moments and their dependence on pressure, is investigated using the Thomas-Fermi model of a gas of interacting electrons. Only the ideal crystal at T = 0 is considered. As a rough approximation the distributions of the charge and spin densities within the Wigner-Seitz cell are taken to be spherically-symmetrical.

1. INTRODUCTION

THE change of the magnetic moment σ_0 of iron with isotropic pressure p has been measured in several experiments (see[1,2]). Kondorskiĭ and Sedov[1] have found that $\Delta\sigma_0/\sigma_0\Delta_p = -3.1 \times 10^{-7}\ \mathrm{atm}^{-1}$. Other ferromagnetic metals behave analogously.

A similar effect, the effect of isotropic pressure on the effective field H^0, measured by means of the Mossbauer effect and nuclear magnetic resonance, has also been investigated in a number of papers. For example, in the work of Moyzis and Drickamer[3] it was found that $\Delta H^0/H^0\Delta p = -1.8 \times 10^{-7}\ \mathrm{atm}^{-1}$. The effective field H^0 is caused mainly by the Fermi contact potential of the spin density at the point at which the nucleus is situated[4]. Usually it is assumed that H^0 increases with the moment of the atom: $H^0 = A\sigma_0$. The origin of the term $\Delta A/A\Delta p = 1.3 \times 10^{-7}\ \mathrm{atm}^{-1}$ remains insufficiently clarified. The compressibility of iron $\Delta V/V\Delta p$ is equal to $-6.098 \times 10^{-7}\ \mathrm{atm}^{-1}$[5].

2. THE INTERACTING-ELECTRON GAS MODEL

The Heisenberg model for ferromagnetism contains atomic moments as parameters and therefore is not a natural model for describing the pressure-dependence of the moments. In the band model one can obtain information about the magnetic behavior of a ferromagnet by considering the change of band structure with lattice parameter. However, the calculations are very laborious and have not yet been carried out for iron.

We shall not use these models. The model of a gas of interacting electrons (Thomas-Fermi model) is convenient for describing the properties of substances on change of pressure. By means of this model, the properties of atoms, molecules and solids can be described with any degree of precision[6]. The merit of the model is that it is easily visualized and gives the simplest interpretation of the correlation. Here we shall use only the simplest approximation; we shall not carry out exact calculations.

The distribution of electrons in a free iron atom was calculated by Wood and Pratt[7] by means of the unrestricted Hartree-Fock method. Here we are interested in the electron distribution in the Wigner-Seitz cell for the metal. The simplest approximation in the interacting-electron gas model corresponds to hydrostatic equilibrium of the electrons; as for the free-electron gas, a relation between the pressure p and the density ρ_q is valid for this equilibrium. If we take $\rho_q(r)$ to be spherically symmetrical, then the calculations for iron give $\rho_q(R) \approx 0.3\ \text{Å}^{-3}$ (here R = 1.22 Å is half the distance between nearest neighbors). Defining the distance R_3, the distance from the nucleus of electrons of principal quantum number n = 3, as the radius of a sphere outside which there are nine electrons, we find $R_3 \approx 0.4$ Å.

The occurrence of atomic moments in certain 3d- and 4f-metals, in contrast to the corresponding 4d-, 5d- or 5f-metals, coincides with a small extent of chemical bonding between the electrons of unfilled shells (this bonding violates Hund's rule if the free atoms form a metallic lattice). The weakness of the chemical bonding in these 3d- and 4f-metals is manifested by the facts that the atomic volumes are relatively large[8], the force constants are small, and the chemical valency is small[8] (e.g., Fe has valency 2 or 3, Ru has valency 3, 4, 6, 8 and Os has valency 4, 6, 8). Thus, the occurrence of atomic moments may be described in the statistical model as the result of intra-atomic and interatomic exchange of electrons from unfilled shells.

Assume that the electron density $\rho_q(r)$ is known with sufficient precision. We shall find the spin density $\rho_s(r) = \rho_{q\uparrow}(r) - \rho_{q\downarrow}(r)$, setting the condition $\rho_s(r) \ll \rho_q(r)$. For this we shall introduce a state of maximum localization of the electron at point $\mathbf{r}_1$ with spin orientation

$$\chi_{\mathbf{r}_1\sigma}(\mathbf{r}_2) = \Big(\sum_n \varphi_{n\sigma}^*(\mathbf{r}_1)\varphi_{n\sigma}(\mathbf{r}_1)\Big)^{-1/2} \sum_n \varphi_{n\sigma}^*(\mathbf{r}_1)\varphi_{n\sigma}(\mathbf{r}_2). \tag{1}$$

The summation is carried out over all occupied states $\varphi_{n\sigma}$, calculated in the Harteee-Fock approximation for the electron Hamiltonian:

$$H = \sum_k \frac{\mathbf{p}_k^2}{2m} + \frac{1}{2}\sum_{k,k'} \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\mathbf{r}_k - \mathbf{r}_{k'}|} + \sum_k V(\mathbf{r}_k), \tag{2}$$

where $V(\mathbf{r}_k)$ is the lattice potential and k labels an electron. In the Thomas-Fermi model, the quantity $\chi_{\mathbf{r}_1\sigma}(\mathbf{r}_2)$ is approximated as follows:

$$\chi_{\mathbf{r}_1\sigma}(\mathbf{r}_2) \approx \frac{4\pi}{h^3\rho_{q\sigma}^{1/2}(\mathbf{r}_1)} \int_0^P \exp\Big(\frac{i}{\hbar}\mathbf{p}(\mathbf{r}_1 - \mathbf{r}_2)\Big)\, p^2\,dp,\quad P = h\Big(\frac{3}{4\pi}\rho_{q,\sigma}(\mathbf{r}_1)\Big)^{1/3}. \tag{3}$$

An electron in the state $\chi_{\mathbf{r}_1\sigma}(\mathbf{r}_2)$ exchanges with electrons in other states but with the same energy.

The exchange may be either intra-atomic or interatomic.

Interatomic exchange causes chemical bonding. Electrons of neighboring atoms tend to have antiparallel spin orientations. Electron pairs arise and the continuous electron exchange results in the average spin density's becoming zero ($\rho_S(\mathbf{r}) = 0$). A measure of the interatomic exchange is the bond energy $E_B(\mathbf{r}_1) = \frac{1}{2}(E_+(\mathbf{r}_1) - E_-(\mathbf{r}_1))$, where

$$E_\pm(\mathbf{r}_1) = \int d^3\mathbf{r}_2 \int d^3\mathbf{r}_4 \chi_\pm^*(\mathbf{r}_2, \mathbf{r}_4) H_{24} \chi_\pm(\mathbf{r}_2, \mathbf{r}_4),$$

$$\chi_\pm(\mathbf{r}_2, \mathbf{r}_4) = \left(2 \pm 2 \left| \int d^3\mathbf{r}_2 \chi^*_{\mathbf{r}_1}(\mathbf{r}_2) \chi_{\mathbf{r}_3}(\mathbf{r}_2) \right|^2\right)^{-1/2} (\chi_{\mathbf{r}_1}(\mathbf{r}_2)\chi_{\mathbf{r}_3}(\mathbf{r}_4) \pm \chi_{\mathbf{r}_1}(\mathbf{r}_4)\chi_{\mathbf{r}_3}(\mathbf{r}_2)),$$

$$H_{24} = \frac{\mathbf{p}_2^2}{2m} + \frac{\mathbf{p}_4^2}{2m} + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\mathbf{r}_2 - \mathbf{r}_4|} + V_{24}(\mathbf{r}_2) + V_{24}(\mathbf{r}_4), \qquad (4)$$

$V_{24}(\mathbf{r})$ is the potential of the lattice and of all the other electrons, $\mathbf{r}_3 = \mathbf{r}_1(R/|\mathbf{r}_1| - 1)$ and the plus and minus signs correspond to parallel and antiparallel orientation of the spins.

Intra-atomic exchange is brought about by the fact that electron spins within the atom tend to line up parallel to each other (Hund's rule). Minimizing the sum E of the kinetic and exchange energies, we obtain the spin density $\rho_{SM}(\mathbf{r})$. As a measure of the intra-atomic exchange, we can take the quantity $E_H(\mathbf{r}_1)$, which is equal to the difference $E - E'(\mathbf{r}_1)$ where the prime corresponds to the distribution $\rho_S'(\mathbf{r})$ which arises on reversal of the spin in the state $\chi_{\mathbf{r}_1\sigma}(\mathbf{r})$.

We shall assume that at a given moment of time t there is an average spin density $\rho_S(\mathbf{r}_1) \geq 0$. In a time Δt, $E_B(\mathbf{r}_1)\Delta t/\hbar$ interatomic exchanges occur, leading to a reduction of the average spin density by $-\rho_S(\mathbf{r}_1)$. The number of intra-atomic exchanges in the time Δt is $E_H(\mathbf{r}_1)\Delta t/\hbar$. This exchange causes the spin density to increase by $(\rho_{SM}(\mathbf{r}_1) - \rho_S(\mathbf{r}_1))$. Intra-atomic exchange with electrons with negative spins occurs more frequently when $\rho_S(\mathbf{r}_1) < \rho_{SM}(\mathbf{r}_1)$ than when $\rho_S(\mathbf{r}_1) = \rho_{SM}(\mathbf{r}_1)$. Here, $\rho_{SM}(\mathbf{r}_1)/\rho_q(\mathbf{r}_1)$ is the fraction of all exchanges when the number of exchanges with positive spins predominates over the number of exchanges with negative spins; with $\rho_S(\mathbf{r}_1)$, this fraction of all exchanges is equal to $\rho_S(\mathbf{r}_1)/\rho_q(\mathbf{r}_1)$.

The intra-atomic and interatomic exchanges together give the change in the average spin density at the point $\mathbf{r}_1$ in time Δt;

$$\rho_s(t + \Delta t) - \rho_s(t) = \frac{E_B}{\hbar}\Delta t(-\rho_s) + \frac{E_H}{\hbar}\Delta t(\rho_{sM} - \rho_s)\frac{\rho_s}{\rho_{sM}}. \qquad (5)$$

If in the stationary case the right-hand side is put equal to zero, then two solutions for $\rho_S(\mathbf{r}_1)$ are obtained

$$\rho_{s_0}(r_1) = 0, \quad \rho_{s_0}(r_1) = \rho_{sM}(r_1)\left(1 - \frac{E_B(r_1)}{E_H(r_1)}\right). \qquad (6)$$

The second solution is stable for the case $E_B/E_H < 1$ but cannot be used for $E_B/E_H > 1$, because ρ_S must be a positive quantity. This result may be simplified, assuming that all electrons in unfilled shells are equivalent. Then for the average moment of the atom we obtain

$$\sigma_0 = 0, \quad \sigma_0 = \sigma_M(1 - E_B/E_H). \qquad (7)$$

Here σ_M is the atomic moment in the state of maximum multiplicity, for which, according to Hund's rule, E has its minimum value.

Assuming that the magnetism sets in only when the interatomic distance becomes greater than a certain critical value (the Mott transition), Goodenough was able to explain the magnetic behavior of many chemical bonds[10]. The change of the magnetic moment with Hund splitting was considered by Mattis[11].

It is possible to estimate the energy E_H in the statistical model in the following way. As in the free iron atom in calculations by the restricted Hartree-Fock method, the kinetic energy need not be different for different distributions of electrons over the 3d-states. If, out of nine positive and five negative spins in states of principal quantum number n = 3 at an average distance R_M of 0.35 Å[7] from the nucleus, one positive spin is flipped, then the average spacing of electrons with one spin alignment changes. According to the free-electron gas model, the change in the exchange energy is 0.48 eV. This order of magnitude is also obtained from spectroscopic data.

The energy E_B may be estimated as follows. If in the free-electron gas both spin orientations were occupied then the gain in energy in comparison with the state in which all spins are parallel would be 5.5 eV, for a density $\rho_q(R) = 0.3$ Å^{-3}. The electron occupies a volume whose surface is, on average, 10.8 Å^2. If we assume that in the crystal the exchange occurs through a surface area $4R^2/16 = 1.18$ Å^2 and treat half the energy difference between the singlet and triplet states as the bond energy per electron, then we obtain $E_B = 0.3$ eV. The value for the bond energy per atom, 0.3×16 eV = 4.8 eV agrees in order of magnitude with the experimental value.

Using the estimates for E_H and E_B and taking into account that $\sigma_M = 4\mu_B$ (this corresponds to the state $3d^6 4s^2$), we obtain for the magnetic moment σ_0 of iron a value $\sim 1.5\mu_B$. It is clear, on the basis of relation (7), why Ru and Os do not have a magnetic moment. For them the Hund splitting is approximately half as large as for the iron and the chemical bonding is considerably greater.

3. RESULTS

The pressure-dependence of the magnetization can be calculated by first of all determining the change with pressure of the electron distribution. From the statistical model it follows, approximately, that the relative change in the electron density $\rho_q(R)$ between the atoms is proportional to the relative volume change with a proportionality constant 1.2. The relative change of the radius R_3 is proportional to one tenth of the relative change of R, $\Delta R/R\Delta p \approx -2 \times 10^{-7}$ atm^{-1}. This means that the relative change of bond energy (proportional to $\rho_q^{2/3}$) increases by 4.8×10^{-7} atm^{-1}, whilst the relative change of the Hund splitting (proportional to $\rho_q^{1/3}$) increases only by 0.2×10^{-7} atm^{-1}.

The pressure dependence of the magnetization is, in accordance with (7)

$$\frac{\Delta\sigma_0}{\sigma_0\Delta p} = \frac{\sigma_M}{\sigma_0}\frac{E_B}{E_H}\left(-\frac{\Delta E_B}{E_B\Delta p} + \frac{\Delta E_H}{E_H\Delta p}\right). \qquad (8)$$

Using the experimental value $\sigma_0 = 2.22\,\mu_B$ and calculating E_B/E_H from formula (7), we find $\Delta\sigma_0/\sigma_0\Delta p = -3.7 \times 10^{-7}$ atm^{-1}.

The change in the effective field H^0 with pressure is explained as follows. Neutron scattering shows that the spin density distributions are similar to the 3d-functions. The inner part of the spin density, close to the nucleus of the atom, polarizes the inner shells. Here the spin density distribution satisfies an r^4 law. If all distances are reduced by a factor $(1 - \Delta R_3/R_3)$ without changing the number of electrons, then the electron density increases by a factor $(1 + 7\Delta R_3/R_3)$. Since the spin density at the nucleus is proportional to this amplitude[12], $\Delta A/A\Delta p = 1.4 \times 10^{-7}$ atm^{-1}.

In the same way the magnetization of other ferromagnetic metals also decreases with increase of pressure, e.g., cobalt behaves similarly to iron. A measurement of $\Delta\sigma_0/\sigma_0\Delta p = -2.9 \times 10^{-7}$ atm^{-1} was made in[1] for nickel. Using the value $\sigma_0 = 0.62\,\mu_B$ for the atomic moment of the metal, the value $\sigma_M = 1\,\mu_B$ (which corresponds to the state $3d^9 4s$) and the value -5.3×10^{-7} atm^{-1} for the compressibility, we obtain $\Delta\sigma_0/\sigma_0\Delta p = 2.6 \times 10^{-7}$ atm^{-1}. For gadolinium, whose moment is also mainly due to the spins of the electrons, the measured value is $\Delta\sigma_0/\sigma_0\Delta p = -1.9 \times - 10^{-7}$ atm^{-1}[13]. Using for the atomic moments of Gd the data $\sigma_0 = 7.12\,\mu_B$ and $\sigma_M = 8\,\mu_B$ (which corresponds to the state $4f^7 5d^1 6s^2$), and for the compressibility the value -25.2×10^{-7} atm^{-1}[13], we have $\Delta\sigma_0/\sigma_0\Delta p \approx 2 \times 10^{-7}$ atm^{-1}.

We shall indicate other effects which can be understood on the basis of this model.

Uranium compounds. In many of its metallic compounds uranium has a magnetic moment which can be detected by means of neutron diffraction. The moment depends strongly on the distance between neighboring atoms of uranium[14]. This is explained by the fact that the covalent bonding between the outer electrons of uranium decreases with increase of the spacing of the atoms and therefore the magnetic moment increases.

Chromium. The linear thermal coefficient of expansion of chromium has a singularity in the vicinity of the Néel point; at this point it becomes negative, and the magnetic moments disappear[16]. The origin of the magnetic moments is connected with the expansion of the crystal lattice, which leads to weakening of the chemical bonding.

Above the Curie point, in the paramagnetic regime, the ferromagnetic elements have a greater effective moment per atom than below the Curie point. In this case the chemical bonding is weakened as a result of the greater thermal expansion[17] and the thermal motion of the atoms.

Alloys. Iron shows an increase in moment on alloying with non-transition metals[18]. This can be explained by the fact that the electrons of these chemical elements enter very weakly into bonding with the 3d-electrons of iron and so do not violate Hund's rule to the same extent. Because of the differences in the energies of the electron states of iron and the impurity, this effect is greater the further the alloying element is from iron in the periodic table (e.g., the series Cu, Ag, Au). Apart from this, the increase of atomic volume also plays a role. When iron is alloyed with transition metals partial bonding occurs between the 3d-electrons of neighboring atoms[19].

Transuranic elements. It is also of interest to investigate whether there exist other chemical elements also having a magnetic phase. The fact that certain transuranic elements, such as Cm, Bk, and Cf, have a large atomic volume and small valency (3) implies the existence of a magnetic phase of the same type as in the rare earth elements. On the other hand, for other elements, such as, e.g., Np and Pu, which have small atomic volumes and high valencies (up to 6), such a phase does not exist.

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