The $4s^2\ 4p^4\ 5s\ {}^4P_{\frac{1}{2}}$ term exhibits deviation from the interval rule, and this accurately obeys the quadratic formula for the interaction which arises when the nucleus has an electrical quadrupole moment. The interaction formula for this term is

$$E = 223 + \tfrac{1}{2} \times 47{\cdot}1C + 0{\cdot}17C(C+1)\ \text{cm.}^{-1} \times 10^{-3}.$$

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Orientation of nuclear spins in metals

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1. INTRODUCTION

In recent years, temperatures down to about 1/100–1/1000 degree absolute have been reached by means of the magnetic cooling method. This method, which was proposed by Debye and by Giauque, consists essentially of isothermal magnetization of a paramagnetic substance, followed by adiabatic demagnetization. Kürti and Simon (1935) have shown that the lowest temperatures which can be reached by this method are proportional to the interaction energy between magnetic dipoles of the substances used. Therefore, in order to reach still lower temperatures, it was proposed by these authors and by Gorter (1934) that the magnetism of atomic nuclei should be used. F. Simon (1939) has recently discussed this idea in greater detail and found that it should be possible to realize it experimentally.

The question now arises of what temperatures can be reached in this way, what times will be necessary and what will be the properties of the nuclear spins at these temperatures.* In this paper we shall investigate these

* Enquiries from Professor Simon on these points stimulated the present work.

questions for metals. Here, the magnetic interaction between the conduction electrons and the nuclei leads to an indirect coupling between the magnetic moments of the nuclei which for many metals is considerably larger than their direct magnetic interaction. We shall show that any metal for which this is the case becomes ferromagnetic with respect to the nuclei. The Curie temperature will be of the order 10^{-6} degree or less, and the temperatures reached by the magnetic cooling method will consequently be of the same order of magnitude. The attainment of such temperatures where the nuclear spins are orientated may be of great importance in nuclear physics.

In insulators the coupling between the nuclear spins is much smaller than in metals, because here their direct magnetic interaction is only slightly influenced by the electrons. Also the times required to reach equilibrium are probably much longer. Metals are therefore the most suitable substances for investigations in the near future, and we shall confine ourselves to them.

2. Interaction between nuclear spins and electrons

In order to investigate the behaviour of nuclear spins in metals we have to find the contributions to the total energy which depend on the direction of these nuclear spins. These contributions arise from two kinds of interaction. The first is the direct magnetic interaction between the nuclear spins. This contribution is *not* characteristic of metals but occurs also in insulators. We shall assume it to be small compared with the second part, which is confined to metals and represents the interaction between nuclear spins and electronic spins. As we shall see in § 6 this condition is fulfilled for most monovalent metals. We shall also restrict ourselves to monovalent metals, i.e. to Cu, Ag, Au and the alkali metals. A free atom of this kind has in the ground state one s-electron in an incomplete shell. The interaction between nuclear moment and electron in such an atom is well known from experimental and theoretical investigations on the hyperfine structure of spectral lines. According to a formula, first derived by Fermi (cf. Bethe 1933), the interaction energy may be written as

$$2C(\mathbf{i}, \mathbf{s}), \tag{1}$$

if the electron is in an s-state. Here $\hbar\mathbf{i}$ is the angular momentum of the nucleus, $\mathbf{s}$ is the spin operator of the electron and C is independent of $\mathbf{i}$ and $\mathbf{s}$ but depends on the value of the electronic wave function near the nucleus. Expression (1) has two proper values according to the two possible orientations of the electronic spin. Their separation determines the hyperfine splitting ϵ:

$$\epsilon = C(i+\tfrac{1}{2}), \quad i \neq 0, \tag{2}$$

which has been measured for all monovalent atoms. In a given atom the hyperfine splitting of an s-state is usually much greater than the splitting of a p, d, ... state, although for such states there is in addition the interaction with the orbital momentum. This is because the magnetic field of the nuclear spin decreases very rapidly with distance, and an s-electron comes much nearer to the nucleus than an electron with orbital angular momentum different from zero.

Now let us consider the corresponding interaction in the metallic state. Here, according to F. Bloch, the wave function of an electron spreads over the whole metal, i.e. an electron has an equal probability $1/N$ of being near any of the N nuclei of the metal. The magnitude of the interaction mainly depends on the behaviour of the wave function very near to the nucleus, where it is approximately the same as in the free atom. Its absolute value may be slightly different, owing to the difference in the normalizations. Consequently the contribution of the nth nucleus to the interaction is

$$\frac{2\alpha}{N} C(\mathbf{i}_n, \mathbf{s}), \tag{3}$$

where $\hbar\mathbf{i}_n$ is the angular momentum of the nth nucleus and α takes account of the different normalization. Thus the total interaction is

$$\frac{2\alpha}{N} C(\Sigma\mathbf{i}_n, \mathbf{s}) = \frac{2\alpha}{N} C(\mathbf{M}, \mathbf{s}),$$

where $\hbar\mathbf{M}$ is the total angular momentum of all nuclei in the metal. As in the free atom, an electronic state splits into two, corresponding to the two possible orientations of the electronic spin. Their separation $\Delta E(M)$ is given by

$$\Delta E(M) = \frac{\alpha}{N} C(M + \tfrac{1}{2}), \quad M \neq 0,$$

analogous to equation (2). Here, $\frac{1}{2}$ can be neglected since, given a certain angular momentum per unit volume, M is proportional to N. Expressing C by the hyperfine splitting ϵ (equation (2)), we find for the splitting of an electronic state in a metal

$$\Delta E(M) = \frac{\alpha\epsilon M}{(i + \frac{1}{2})N}. \tag{4}$$

We thus see that, owing to the interaction between electronic and nuclear spins, an electronic state splits into two, corresponding to anti-parallel spin directions, just as happens under the influence of an external magnetic

field H, where the splitting is $2\mu H$, μ being the Bohr magneton. The interaction with an external magnetic field

$$H(M) = \alpha\epsilon M/2\mu(i+\tfrac{1}{2})N \tag{5}$$

would, therefore, give the same contribution to the total energy as does the nuclear spin electronic spin interaction, provided that we consider the action of the field on the *electronic spins* only. The total interaction energy $U(M)$ is, therefore, given by

$$U(M) = -\tfrac{1}{2}\chi_p H^2(M)\, V, \tag{6}$$

where V is the volume and χ_p is the *paramagnetic* susceptibility of the electrons.

If all the nuclear spins are parallel, the "effective" magnetic field $H(M)$ is rather strong because s-electrons, as mentioned above, come very near to the nucleus. For Cu, for instance, it is about 5000 G. There exists, of course, also a diamagnetic interaction between electrons and nuclear spins. For this kind of interaction, as far as it depends on the *direction* of the nuclear spins, the effective magnetic field is much smaller than $H(M)$, so that the contribution to the total interaction is negligible.*

Inserting (5) into (6) we find

$$U(M) = -\tfrac{1}{8}\chi_p \frac{\alpha^2\epsilon^2 M^2 V}{\mu^2(i+\tfrac{1}{2})^2 N^2}. \tag{7}$$

Assuming the electrons to behave like free electrons with an effective mass m^*, χ_p, first calculated by Pauli, may be written as (cf. Fröhlich 1936)

$$\chi_p = \frac{3}{2}\frac{\mu^2 n}{\zeta}, \tag{8}$$

* There are two diamagnetic parts: first, the diamagnetism of closed shells. Here the interaction of a nuclear spin with its own closed shell is independent of the *direction* of the spin and hence does not give a contribution to the spin-dependent interaction. The interaction with neighbouring shells is very small indeed, even compared with the direct interaction between nuclear spins which has already been neglected. In fact it is just a part of the correction which has to be made to this direct interaction because the interaction takes place in a medium with a certain magnetic susceptibility, and not *in vacuo*. In Cu the effective magnetic field is of the order of 1 G or less. There is secondly the diamagnetism of the conduction electrons (Landau diamagnetism) which even if it had to be considered would only reduce equation (6) to two-thirds of its value (cf. for example, Fröhlich 1936). But in fact for the part of the interaction which depends on the direction of the nuclear spins, the effective magnetic field should again be smaller than $H(M)$. For only an interaction with the orbital momentum of the electron can depend on the *direction* of nuclear spin. As mentioned above, this leads to a smaller interaction than that considered in the text.

where $$\zeta = \frac{\hbar^2}{2m^*}(3\pi^2 n)^{\frac{2}{3}} \tag{9}$$

is the energy region occupied by the conduction electrons, and

$$n = N/V \tag{10}$$

is the number of atoms per unit volume.

Inserting (8) and (10) into (7), we find for the interaction energy

$$U(M) = -\frac{3\alpha^2\epsilon^2}{16}\frac{M^2}{\zeta(i+\frac{1}{2})^2 N}. \tag{11}$$

This means that the state in which all nuclear spins are parallel, i.e. in which M has its highest value, has the lowest energy.

3. Thermal properties

In order to derive the thermal properties of the metal, we calculate its free energy F, which, according to a well-known theorem is given by

$$e^{-F/kT} = \sum_{\text{nuclei}} \sum_{\text{electrons}} e^{-E_n/kT}. \tag{12}$$

Here E_n is the energy of the nth quantum state of the whole metal. n represents a whole series of indices, including the quantum numbers of all electrons and the spin directions of all nuclei. The sum has to be carried out over all states of the electrons and of the nuclear spins. Let us first carry out the sum over all electronic states for a fixed state of nuclear spins, leading to a nuclear angular momentum $\hbar M$. Then, according to the results of § 2, the energy states are the same as they would be if the electron spins were not in interaction with the nuclei, but instead with a magnetic field of strength $H(M)$, given by equation (5). Therefore

$$\sum_{\text{electrons}} e^{-E_n/kT} = e^{-F(M)/kT}, \tag{13}$$

where $F(M)$ is the free energy of the electrons in the magnetic field $H(M)$, i.e. since the paramagnetic susceptibility χ_p of the electrons does not depend on temperature (cf. equation (7))

$$F(M) = F_0 - \tfrac{1}{2}\chi_p H^2(M)\, V = F_0 + U(M). \tag{14}$$

Here F_0 is the free energy of the electrons without a magnetic field. F_0 depends on T, but not on M. Inserting (13) and (14) into (12) we obtain

$$e^{-(F-F_0)/kT} = \sum_{\text{nuclei}} e^{-U(M)/kT}. \tag{15}$$

Now we remark that, since according to (7) $U(M) \sim -M^2$, $F - F_0$ is identical with free energy of a ferromagnetic substance in Weiss's theory of ferromagnetism (cf. Stoner, 1934). Let F_{ferro} be the free energy according to this theory; then the total free energy becomes

$$F = F_0 + F_{\text{ferro}}. \tag{16}$$

Just as in a ferromagnetic substance, we consequently have to expect at a temperature θ a phase transition of the second order, a so-called λ-point or Curie point characterized by a jump in the specific heat leading up to values of the order of the Boltzmann constant. θ is given by the Weiss theory (cf. Stoner 1934) as (cf. equations (5) and (6))

$$k\theta = -\frac{2i(i+1)}{3}\frac{U(M)N}{M^2} = \frac{1}{12}\frac{i(i+1)}{(i+\frac{1}{2})^2}\chi_p\frac{\alpha^2\epsilon^2}{\mu^2 n}, \tag{17}$$

or making use of the theoretical value (8) for χ_p

$$k\theta = \frac{1}{8}\frac{i(i+1)}{(i+\frac{1}{2})^2}\frac{\alpha^2\epsilon^2}{\zeta} \simeq \frac{1}{8}\frac{\alpha^2\epsilon^2}{\zeta}. \tag{18}$$

4. Magnetic properties

In order to derive the magnetic properties, we have to calculate the free energy in the presence of an external magnetic field H. This can be done by a method similar to that of § 3, replacing the internal field $H(M)$ by the total field $H + H(M)$ and adding the diamagnetic interaction and the direct interaction between H and nuclear spins. Thus we have to replace $U(M)$ by

$$U(M,H) = -\tfrac{1}{2}\chi_p(H+H(M))^2 V + \tfrac{1}{2}\chi_d H^2 V - \mu_n\frac{MH}{i}.$$

Here χ_d (> 0) is the diamagnetic susceptibility. Its sign is chosen so that the total susceptibility χ is given by

$$\chi = \chi_p - \chi_d;$$

μ_n is the magnetic moment of a nucleus.

Using equation (6) reduces the above expression to the form

$$U(M,H) = U(M) - \tfrac{1}{2}\chi H^2 V - \mu^* MH/i, \tag{19}$$

where

$$\mu^* = \mu_n + \chi_p H(M)\, iV/M. \tag{20}$$

According to expression (19) the metal shows its ordinary susceptibility χ on which the ferromagnetism of the nuclei is superposed. The nuclear spins

behave as if they had not their magnetic moment μ_n but an effective magnetic moment μ^*. Its meaning can easily be understood if we consider the metal without a magnetic field at a temperature $T<\theta$. Then the total magnetic moment consists of that of the nuclear spins plus the contribution of the electrons, which is $\chi_p H(M)$. $|\mu^*-\mu_n|/\mu_n$ is usually very small; its order of magnitude is 10^{-2}.

5. Time of relaxation

The magnetic cooling method can only be carried out successfully if after the application of a magnetic field at the initial temperature T_i thermodynamic equilibrium is established in a reasonable time. Heitler and Teller (1936) have already considered this question. They show that a nucleus can change its spin direction when it collides with an electron, the total angular momentum being conserved. They calculate the probability w that such a transition will take place in unit time from the well-known quantum mechanical formula

$$w = 4\pi^2 |W|^2 \rho/h, \tag{21}$$

where W is the matrix element of the interaction between nuclear spin and electron. ρ is the density of states per energy interval dE of the electrons near the top of the Fermi distribution ζ. They assume $W \sim \epsilon$, the hyperfine structure splitting, and find

$$w \simeq \epsilon^2 k T_i/h\zeta^2. \tag{22}$$

In the derivation of this expression it was assumed that because of the Pauli principle only electrons in an interval of the order kT_i near the top of the Fermi distribution can make transitions. This is, however, only true if $2\mu_n H < kT_i$, H being the external magnetic field. If $2\mu_n H > kT_i$, electrons in an interval $2\mu_n H$ will be able to make collisions in which their spin changes its direction. This is because in such a collision the nucleus (assuming $i=\frac{1}{2}$) loses magnetic energy $2\mu_n H$ which has to be taken up by the electron as kinetic energy. It should be mentioned that the electrons are assumed to be in equilibrium with the magnetic field. We then find after a simple calculation

$$w = \frac{9\pi^2 \epsilon^2 \mu_n H}{2 h\zeta^2}, \quad \mu_n H \gg kT_i. \tag{23}$$

If the condition $\mu_n H \gg kT_i$ is no longer fulfilled, w becomes larger; for $\mu_n H \ll kT_i$, $2\mu_n H$ has to be replaced by kT_i. Our formula then becomes identical with Heitler and Teller's formula (22), apart from a numerical factor which they have not considered.

6. Discussion

In the previous sections we found that the nuclei of a monovalent metal should become ferromagnetic at a temperature θ given by equations (17) or (18), provided that the direct interaction between the nuclear spins is sufficiently small. This direct interaction $U'(M)$ may be estimated as follows: Let H' be the magnetic field produced by all the nuclei except one, say the nth, whose angular momentum is $\hbar\mathbf{i}_n$. Then $\frac{\mu_n}{i_n}(\mathbf{i}_n, \mathbf{H}')$ is its energy. Thus the total interaction energy is given by

$$U'(M) = -\frac{1}{2}\frac{\mu_n}{i}(\mathbf{M}, \mathbf{H}').$$

Supposing that the Lorentz formula can be applied approximately, H' is given by

$$H' = \frac{4\pi}{3}\frac{\mu_n M}{iV},$$

i.e.

$$U'(M) = -\frac{2\pi}{3}\frac{\mu_n^2 M^2}{i^2 V}.$$

Thus the ratio γ of the two interactions, which we have assumed to be small compared to one, is, using equation (11)

$$\gamma = \frac{U'(M)}{U(M)} = \frac{32\pi}{9}\left(\frac{i+\frac{1}{2}}{i}\right)^2 \frac{\mu_n^2 n\zeta}{\alpha^2\epsilon^2}. \tag{24}$$

In the following table we give the values of the Curie temperature θ (18) for those monovalent metals for which the condition $\gamma \ll 1$ holds. We also give in this table the nuclear spin i, the magnetic moment μ_n in terms of the nuclear magneton μ_0, the hyperfine structure splitting† ϵ in cm.$^{-1}$, and the ratio $f = m/m^*$ of the real to the effective electronic mass, used‡ in order to calculate ζ according to equation (9). The factor α was for Cu found to be about 1·7 according to wave functions kindly provided by Dr K. Fuchs (cf. also Fuchs 1935). For the other metals no such wave functions were available. We used $\alpha = 1$ which for the alkali metals should be very near to the actual value, owing to their large atomic volume.

† Cf. Elliott and Wulff (1939); Jackson and Kuhn (1937, 1939); Tolanski and Forester (1938).

‡ This ratio f is taken from Fröhlich (1936), table 9, where it is calculated from the experimental susceptibilities of the metals. These f-values are rather smaller than f-values obtained in other ways, which indicates that the interaction between the metal electrons plays some role in determining the susceptibility.

	Cu 63 and 65	Ag 107	Ag 109	Au 197	K 39	Rb 85	Rb 87	Cs 133
i	3/2	1/2	1/2	3/2	3/2	5/2	3/2	7/2
μ_n/μ_0	2·7	0·1	0·2	0·2	0·37	1·3	2·6	2·5
ϵ in cm.$^{-1}$	0·40	0·04	0·08	0·22	0·015	0·10	0·23	0·31
f	0·4	0·5	0·5	0·55	0·6	0·65	0·65	0·9
$\theta \times 10^6$ °	4	10^{-2}	4×10^{-2}	0·4	4×10^{-3}	0·2	1	2
γ	0·07	0·04	0·04	0·00	0·2	0·03	0·03	0·01

This table shows that the Curie temperature for nuclear ferromagnetism is of the order of 10^{-6} degree or less. The entropy which a metal has at $T > \theta$ owing to the disorder of the nuclear spins will decrease rapidly as T becomes smaller than θ, and the specific heat will have values of the order of the Boltzmann constant. The entropy of the electrons and of the lattice vibrations is negligibly small at such temperatures. In applying the magnetic cooling method, the number of orientated nuclear spins should, therefore, remain constant when the external field is removed. One may thus hope to reach by this method temperatures below, but of the order of magnitude of, the Curie temperature θ.

The saturation moment of these ferromagnetic metals is of the order of 1/1000 of the magnetic moment of an ordinary ferromagnetic metal, and should, therefore, be easily detectable. In an external magnetic field H this moment is (cf. § 4) superposed by the ordinary moment χHV due to the ordinary magnetic susceptibility χ of the metal. In a normally diamagnetic metal, as Cs or Cu, there exists, therefore, a field strength where the nuclear ferromagnetism and the ordinary diamagnetism just cancel. These fields are of the order of 10^6 G, so that under normal conditions the nuclear ferromagnetism is preponderant.

In the application of the magnetic cooling method, it is important that the time τ which a nuclear spin requires in order to be orientated in the field shall be of a reasonable order of magnitude. This is actually the case. According to § 5, τ is given by $1/w$. w decreases with increasing temperature. Its lower limit for $T \to 0$ is given by equation (23). In a field of 10^4 G, this leads for Cu to an *upper limit* of about 1 sec. for τ, an order of magnitude already derived by Heitler and Teller (1936) for a temperature of 0·1°.

In conclusion we should like to thank Professor F. Simon, Dr N. Kürti and Dr H. Kuhn for many interesting discussions.

SUMMARY

In connexion with the possible use of nuclear magnetism for the magnetic cooling method, the behaviour of the nuclear spins of monovalent metals at very low temperatures is investigated theoretically. It is shown that, owing to the interaction between the nuclear spins and the conduction electrons, the nuclei of most monovalent metals should become ferromagnetic at temperatures of the order of 10^{-6} degree. The Curie temperature θ for this nuclear ferromagnetism is approximately given by

$$k\theta \sim \frac{1}{8}\frac{\epsilon^2}{\zeta}$$

where ϵ is the hyperfine structure splitting of the free atom, and ζ is the energy region occupied by the conduction electrons. Temperatures of this order of magnitude should be attainable by an application of the magnetic cooling method.

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