EFFECT OF ELECTRON DIAMAGNETISM ON THE NUCLEAR MAGNETIC RESONANCE FREQUENCIES IN METALS

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Submitted to JETP editor June 24, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) **46**, 593-597 (February, 1964)

The effect of electron diamagnetism on the Knight shift is taken into account in the quasi-particle approximation for an arbitrary dispersion law. The oscillatory dependence of the diamagnetic part of the Knight shift on the magnetic field strength is derived. The oscillation amplitude is proportional to $H^{1/2}$. An estimate of the oscillating part of the Knight shift σ_{osc} indicates that $\sigma_{osc} \sim 10^{-3}\,\sigma$ for magnetic fields of the order of 10^4 Oe. As in the case of the deHaas—van Alphen effect, an experimental determination of the period and amplitude of the oscillations should be sufficient for reconstructing the Fermi surface.

ALONG with a paramagnetic Knight shift,[1] which is caused by a magnetic interaction between the nucleus and the conduction electrons, there is also a diamagnetic shift in metals as a consequence of the orbital motion of the conduction electrons in the magnetic field. Das and Sondheimer[2] first considered the diamagnetic contribution to the Knight shift for free electrons and showed that on taking into account the quantization of the electronic orbits in a magnetic field there should take place an oscillating dependence of the diamagnetic part of the Knight shift on magnetic field. The amplitude of the oscillations in the free electron approximation diminished with increasing magnetic field as $H^{-1/2}$. Stephen[3] pointed out that the oscillating character has also the usual paramagnetic Knight shift, since the density of states is an oscillating function, but these oscillations are significantly less than the diamagnetic ones. In [3] the amplitude of the oscillations of the diamagnetic Knight shift does not depend on magnetic field.

The present paper gives a calculation of the diamagnetic contribution to the Knight shift in the quasi-particle approximation for an arbitrary dispersion law. A semi-classical case is considered, in which the condition $\hbar\omega \ll \zeta$ is fulfilled, where ω is the frequency of rotation of the electron in the magnetic field, and ζ is the chemical potential.

CALCULATION OF THE KNIGHT SHIFT

The Hamiltonian of the interaction between the nucleus and the conduction electrons of the s-type in an external field H has the form (see [4])

$$\mathcal{H} = \gamma\hbar I_z H - \frac{8\pi}{3}\gamma\hbar \mathbf{I}\sum_k \boldsymbol{\mu}_k \delta(\mathbf{r}_k). \tag{1}$$

Here μ_k is the magnetic moment of the k-th conduction electron, and the summation is carried out over all conduction electrons. Considering that the magnetic moment of the electrons is negative, we have for the energy of interaction

$$E_m = -\gamma\hbar m_I H + \frac{16\pi}{3}\beta\gamma\hbar m_I \sum_k |\psi_k(0)|^2 m_{sk}, \tag{2}$$

where $m_I = \langle I_z \rangle$, $m_s = \langle S_z \rangle$ and $|\psi_k(0)|^2$ is the probability density of the k-th electron at the nucleus.

We obtain from Eq. (2) for the Knight shift

$$\sigma = \frac{16\pi\beta}{3H}\sum_k |\psi_k(0)|^2 (-m_{sk}). \tag{3}$$

For simplicity, we limit our consideration to a model of free electrons in a uniform magnetic field.[5] Then the wave function should be written in the form

$$\psi(x, y, z) = \frac{1}{\sqrt{L_1 L_3}}\varphi_{n, p_z}\left(y + \frac{cp_x}{eH}\right)\exp\{i(xp_x + zp_z)/\hbar\},$$

$$\int_{-\infty}^{\infty} |\varphi(y)|^2 dy = 1,$$

where L_1 and L_3 are the dimensions of the sample in the direction of the x and z axes. The number of states in the interval $\Delta p_x \Delta p_z$ for a given value of quantum number n and a given direction of spin is, in the semiclassical approximation, equal to

$$(2\pi\hbar)^{-2} L_1 L_3 \Delta p_x \Delta p_z.$$

By transforming in Eq. (3) from a summation over conduction electrons to a summation over all possible states of an individual electron and letting the dimensions of the sample L_1 and L_3 go to infinity, we replace the sum over the possible values of p_x and p_z by an integral. Then

$$\sigma=\frac{4\beta e}{3\pi\hbar^2 c}\sum_{\text{spin}}(-m_s)\sum_{n=0}^{\infty}\int_{-\infty}^{\infty}dp_z f\left(\frac{E_n(p_z)-\varepsilon}{\Theta}\right). \quad (4)$$

Here $f(x)$ is the Fermi distribution, $\epsilon=\zeta\mp\beta H$, and ζ is the chemical potential.

It is easy to verify, using the Poisson summation formula,[6] that Eq. (4) can be converted to the following form:

$$\sigma=\frac{4\beta e}{3\pi\hbar^2 c}\sum_{\text{spin}}(-m_s)\left\{\int_{-1/2}^{\infty}dn\int_{-\infty}^{\infty}dp_z f\left(\frac{E_n-\varepsilon}{\Theta}\right)\right.$$
$$\left.+2\,\mathrm{Re}\sum_{k=1}^{\infty}\int_{-1/2}^{\infty}dn\int_{-\infty}^{\infty}dp_z f\left(\frac{E_n-\varepsilon}{\Theta}\right)\exp(2\pi ink)\right\}. \quad (5)$$

We shall show that the first term in curly brackets corresponds to the Knight shift caused by the paramagnetism of the conduction electrons. The dependence of the energy of a quasi-particle in the magnetic field on the quantum number n has, in the semi-classical approximation, the form (see [7])

$$S(E,p_z)=(n+\gamma)\,2\pi\hbar eH/c \quad (0<\gamma<1). \quad (6)$$

Then the first term in curly brackets in (5) equals

$$J_1=\frac{c}{2\pi eH\hbar}\int_0^{\infty}dEf\left(\frac{E-\varepsilon}{\Theta}\right)\frac{d}{dE}\int_{S>0}S(E,p_z)\,dp_z.$$

From this, in a way similar to that used by I. Lifshitz and Kosevich[7] to derive their Eq. (2.8), we obtain

$$J_1=(c\beta/2\pi e\hbar)\,\partial U(\zeta)/\partial\zeta.$$

Therefore for the Knight shift caused by the first term in the curly brackets in (5), we have

$$\sigma_p=\frac{8\pi}{3}\beta^2\frac{2}{(2\pi\hbar)^3}\frac{\partial U(\zeta)}{\partial\zeta}.$$

Since the expression $2\beta^2(2\pi\hbar)^{-3}\,\partial U(\zeta)/\partial\zeta$ is the paramagnetic part of the susceptibility of a gas, we have finally

$$\sigma_p=\tfrac{8}{3}\pi\chi_p.$$

The same expression for the Knight shift was obtained in [2] by considering only paramagnetic effects.

We go over now to a consideration of the diamagnetic part σ_d of the Knight shift, which is described by the second term in Eq. (5),

$$\sigma_d=\frac{4\beta e}{3\pi\hbar^2 c}\sum_{\text{spin}}(-m_s)\,2\,\mathrm{Re}\sum_{k=1}^{\infty}\int_{-1/2}^{\infty}dn\int_{-\infty}^{\infty}dp_z f\left(\frac{E_n-\varepsilon}{\Theta}\right)$$
$$\times\exp(2\pi ink). \quad (7)$$

Using Eq. (6), we transform the integrals appearing in this expression to the form

$$J_k=\frac{c}{2\pi e\hbar H}\int_0^{\infty}dEf\left(\frac{E-\varepsilon}{\Theta}\right)\int_{S>0}dp_z\frac{\partial S}{\partial E}$$
$$\times\exp\left\{\frac{ikc}{e\hbar H}S(E,p_z)-2\pi ik\gamma\right\}.$$

An integral of this type was calculated in the paper of Lifshitz and Kosevich.[7] Without repeating the corresponding calculations, we write*

$$J_k=-i\left(\frac{e\hbar H}{2\pi c}\right)^{1/2}\frac{1}{k^{3/2}}\left|\frac{\partial^2 S(\varepsilon,p_z)}{\partial p_z^2}\right|_m^{-1/2}\Psi(k\lambda)$$
$$\times\exp\left\{\frac{ikc}{e\hbar H}S_m(\varepsilon)-2\pi ik\gamma\mp\frac{\pi i}{4}\right\},$$
$$\Psi(k\lambda)=\frac{k\lambda}{\operatorname{sh}k\lambda},\quad \lambda=\frac{\pi c\Theta}{e\hbar H}\frac{\partial S_m(\varepsilon)}{\partial\varepsilon},$$

where S_m is the area of the extremal section. Substituting this expression for J_k in Eq. (7), we obtain for the oscillating part of the Knight shift

$$\sigma_{osc}=\frac{8\beta}{\sqrt{2\pi}\,3\pi\hbar^3}\left(\frac{e\hbar}{c}\right)^{3/2}\sqrt{H}\sum_{\text{spin}}(-m_s)\sum_{k=1}^{\infty}\frac{\Psi(k\lambda)}{k^{3/2}}$$
$$\times\left|\frac{\partial^2 S(\varepsilon,p_z)}{\partial p_z^2}\right|_m^{-1/2}\sin\left(\frac{kc}{e\hbar H}S_m(\varepsilon)-2\pi k\gamma\mp\frac{\pi}{4}\right).$$

To accomplish the sum over spin we expand $S_m(\epsilon)$ in the argument of the sine function in powers of βH, limiting the expansion to terms of the first order; in the remaining coefficients we can replace ϵ with ζ_0, the chemical potential in the absence of magnetic field. The final expression for the oscillating part of the Knight shift has the form

$$\sigma_{osc}=\frac{8\beta}{3\pi\sqrt{2\pi}}\left(\frac{e}{c\hbar}\right)^{3/2}\sqrt{H}\left|\frac{\partial^2 S}{\partial p_z^2}\right|_m^{-1/2}$$
$$\times\sum_{k=1}^{\infty}\frac{\Psi(k\lambda)}{k^{3/2}}\cos\left[\frac{kc}{e\hbar H}S_m(\zeta_0)\mp\frac{\pi}{4}-2\pi k\gamma\right]\sin\left[\frac{k}{2m_0}\frac{\partial S(\zeta_0)}{\partial\zeta_0}\right]. \quad (8)$$

From Eq. (8) it follows that the amplitude grows as $H^{1/2}$. In order to estimate the order of magnitude of the amplitude of the oscillations in the Knight shift, we make use of the expression for the oscillating part of the magnetic susceptibility of metals[7]:

*sh = sinh.

$$M_{osc}=-\frac{4}{(2\pi)^{5/2}}\left(\frac{e}{c\hbar}\right)^{3/2}S_m(\zeta)\left|\frac{\partial^2 S(\zeta,p_z)}{\partial p_z^2}\right|_m^{-1/2}\left|\frac{\partial S_m(\zeta)}{\partial\zeta}\right|^{-1}\sqrt{H}$$
$$\times\sum_{k=1}^{\infty}\frac{\Psi(k\lambda)}{k^{3/2}}\sin\left[\frac{kc}{e\hbar H}S_m(\zeta)\mp\frac{\pi}{4}-2\pi k\gamma\right]$$
$$\times\cos\left[\frac{k}{2m_0}\frac{\partial S_m(\zeta)}{\partial\zeta}\right]. \quad (9)$$

Comparing (8) and (9), we have in order of magnitude

$$\sigma_{osc}\approx\frac{8\pi\beta}{3}\frac{\partial S_m(\zeta)}{\partial\zeta}\frac{1}{S_m(\zeta)}M_{osc}.$$

Since the oscillations of the magnetic susceptibility are of the order of the magnetic susceptibility itself, we can say that $M_{osc}\sim\chi_p H$. Then

$$\frac{\sigma_{osc}}{\sigma_p}\approx\beta H\frac{\partial S_m(\zeta)}{\partial\zeta}\frac{1}{S_m(\zeta)}\approx\frac{\beta H}{\zeta}.$$

If $\zeta\sim10^{-13}$, $H\sim10^4$ Oe, then $\sigma_{osc}/\sigma_p\sim10^{-3}$. For Li^7 σ_p is equal in order of magnitude to 3×10^{-5} and increases to 1.2×10^{-2} for lead; hence the experimental measurement of oscillations of the Knight shift is perfectly real.

For a square law of dispersion, Eq. (8) takes the following form:

$$\sigma_{osc}=\frac{8\Theta\beta m}{3\sqrt{H}}\left(\frac{e}{c\hbar}\right)^{1/2}$$
$$\times\sum_{k=1}^{\infty}\frac{(-1)^k\cos\left(2\pi mk\zeta c/e\hbar H\mp\frac{\pi}{4}\right)\sin(k\pi m/m_0)}{k^{1/2}\,\mathrm{sh}\,(2\pi^2kc\,\Theta m/e\hbar H)}. \quad (10)$$

At absolute zero, or for very strong magnetic fields, when $\lambda\ll1$, the function $\Psi(k\lambda)$ in Eq. (8) can be replaced by unity. Then

$$\sigma_{osc}=\frac{8\beta}{3\pi\sqrt{2\pi}}\left(\frac{e}{c\hbar}\right)^{3/2}\sqrt{H}\left|\frac{\partial^2 S}{\partial p_z^2}\right|_m^{-1/2}$$
$$\times\sum_{k=1}^{\infty}\frac{1}{k^{3/2}}\cos\left[\frac{kc}{e\hbar H}S_m(\zeta)\mp\frac{\pi}{4}-2\pi k\gamma\right]$$
$$\times\sin\left[\frac{k}{2m_0}\frac{\partial S_m(\zeta)}{\partial\zeta}\right]. \quad (11)$$

For small fields or high temperatures $\lambda\gg1$. In this case $\Psi(k\lambda)\sim2k\lambda e^{-k\lambda}$. This limits us to only one term in Eq. (8), k = 1. Thus,

$$\sigma_{osc}=A(H,\zeta)\cos\left[\frac{c}{e\hbar H}S_m(\zeta)\mp\frac{\pi}{4}-2\pi\gamma\right]. \quad (12)$$

Here

$$A(H,\zeta)=\frac{16\beta\Theta e^{-\lambda}}{3\hbar^3\sqrt{2\pi H}}\left(\frac{e\hbar}{c}\right)^{1/2}\frac{\partial S_m(\zeta)}{\partial\zeta}\left|\frac{\partial^2 S_m}{\partial p_z^2}\right|_m^{-1/2}$$
$$\times\sin\left[\frac{1}{2m_0}\frac{\partial S_m(\zeta)}{\partial\zeta}\right].$$

In conclusion, we remark that integration in Eq. (7) over p_z in the vicinity of the ends of the interval $S(E, p_z) = 0$ gives a non-oscillating diamagnetic part of the Knight shift. In calculations it is necessary, however, to take into account that the neighborhood of the ends of the interval $S(E, p_z) = 0$ corresponds to small quantum numbers n, and the semiclassical approximation (6) cannot be used. A rigorous calculation of the non-oscillating diamagnetic part of the Knight shift is possible only for a square law of dispersion, when the semi-classical energy levels (6) coincide with the exact levels for all n.

It turned out that for a square law of dispersion the non-oscillating diamagnetic part of the Knight shift equalled zero.

In conclusion, we express our thanks to M. Ya. Azbel' for a helpful discussion of this work.

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Translated by L. M. Matarrese
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