Oscillations of the chemical potential and the equation of state for beryllium

N. E. Alekseevskiĭ and V. I. Nizhankovskiĭ

Institute of Physical Problems, Academy of Sciences of the USSR

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An attempt was made to detect oscillations of the chemical potential of beryllium associated with variations in the density of states in a quantized magnetic field. No oscillations were detected from voltage traces recorded across a measuring capacitor with a Be single crystal as one of its plates, and it is deduced that their amplitude is at least an order of magnitude less than expected. The result is attributed to cancellation of the changes in the chemical potential associated with oscillations in the density of states and with magnetostriction (volume changes). Such cancellation can occur if the compressibility of beryllium is determined primarily by the conduction electrons.

Lifshitz and Kosevich[1] first observed that the chemical potential of the electrons might oscillate when metals are placed in strong magnetic fields. These oscillations are similar in nature to the more familiar de Haas–van Alfven and Shubnikov–de Haas oscillations in metals and are associated with variations in the density of electron states as the Landau levels cross the Fermi surface. The chemical potential oscillations are determined primarily by the sheet of the Fermi surface giving the dominant contribution to the oscillations in the magnetization; the other sheets act as "reservoirs" and damp the oscillations in the chemical potential. The amplitude μ_{osc} of the latter is thus proportional to the amplitude $|\mathbf{M}_{\text{osc}}|$ of the magnetization oscillations and inversely proportional to the density $n(\varepsilon_F)$ of the electron states on the Fermi surface:

$$\mu_{\text{osc}} = -\frac{m^* c}{2e\hbar F n(\varepsilon_F)} \mathbf{M}_{\text{osc}} \mathbf{H}, \qquad (1)$$

Here F is the oscillation frequency of the magnetization and H is the magnetic field.[1,2]

Estimates predict an extremely small oscillation amplitude $\mu_{\text{osc}} \sim 10^{-9}$ V for the alkali and precious metals for $H = 80$ kOe and $T = 4.2$ K. Nevertheless, the oscillations have been observed for bismuth,[3] lead,[4] zinc[5], and antimony.[6] However, the measured amplitudes were substantially higher than expected and are comparable to the spacing $\hbar\omega_c \sim 10^{-3}$ V between the Landau levels.

There are two reasons for our interest in measuring μ_{osc} for beryllium in the present paper. First, the very low density of states $n(\varepsilon_F)$ at the Fermi level[7] and the large amplitude of the magnetization oscillations[8] suggest that μ_{osc} for beryllium should be larger than for other metals. Second, we recently found[9] that the thermal emf for Be and the phase of the magnetic breakdown oscillations in the resistance have an unusual dependence on the angle α between the magnetic field and the hexagonal crystal axis. The larger additional phase shift $\delta\varphi \sim 1$ of the oscillations as $\alpha \to 0$ cannot be attributed to the geometry of the Fermi surface for Be or to the Shoenberg effect (the nonlinear dependence of the induction **B** in the crystal on the applied magnetic field **H**).

This anomalous behavior could be a consequence of oscillations in the chemical potential. Indeed, according to Ref. 1 the correction $\delta\varphi$ to the phase of the oscillations is given by the ratio

$$\delta\varphi/2\pi \approx \mu_{\text{osc}}/\hbar\omega_c,$$

where $\hbar\omega_c$ is the spacing between the Landau levels; thus $\delta\varphi$ can be ~ 1 if $\mu_{\text{osc}} \sim \hbar\omega_c$.

The Fermi surface for beryllium is known accurately enough so that the expected amplitudes of the magnetization and chemical potential oscillations can be reliably estimated.[10] If **H** is parallel to the [0001] direction, the magnetization oscillations are determined by three extremal cross sections ("cigars") of the electron sheets of the Fermi surface; one of the sheets (S_1) is central, while the other two noncentral sheets (S_2) are symmetric about S_1. The corresponding magnetization oscillation frequencies for these sheets are $F_1 = 9.42$ MHz and $F_2 = 0.72$ MHz. Because of the small difference between F_1 and F_2, the amplitude of the magnetization oscillations is modulated at the beat frequency F_2–F_1 and passes through a maximum where the oscillations caused by S_1 and S_2 are in phase; the field interval 75 Oe$\leqslant H \leqslant$80 kOe was chosen to satisfy the latter condition.

We assume in estimating $\partial^2 S/\partial p_z^2$ that

$$S(p_z) = S_1 + (S_2 - S_1)\sin^2\left(\frac{\pi}{2}\frac{p_z}{p_{z0}}\right),$$

where p_{z0} is the distance between the extremal sections S_1 and S_2. We then find that $\partial^2 S/\partial p_z^2 = \pi^2(S_2 - S_1)/2p_{z0}^2 \approx 0.24$.

We estimate the Dingle temperature by measuring the magnetoresistance in weak fields. In this case $\rho(H)/\rho(0) \approx 1 + (\omega_c\tau)^2$, and the field H_1 for which $\rho(H_1) = 2\rho(0)$ corresponds to the condition $\omega_c\tau = 1$. The equivalent Dingle temperature is therefore given by $k_B T_D = \hbar\omega_c(H_1)$; for our crystals $H_1 \approx 2$ kOe and $T_D \approx 1.3$ K.

If we substitute $m^* = 0.17m$, $\overline{F} = 9.5$ MHz, and the above parameter values into the expression for the de Haas–Alfven effect,[11] we get the result $|M_{\text{osc}}| \approx 3.2$ Gauss for the amplitude of the magnetization oscillations at $T = 4.2$ K, $H = 80$ kOe. We note that a similar estimate for $|M_{\text{osc}}|$ at $T = 4.2$ K and $H = 20$ kOe agrees closely with the results of direct measurements[12].

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The density of states at the Fermi level for beryllium is $n(\varepsilon_F) = 0.85$ state/at. $\mathrm{Ry} = 4.84\cdot10^{33}$ erg^{-1}; Eq. (1) then yields the estimate $|\mu_{\mathrm{osc}}| \approx 17.4\,\mu\mathrm{V}$ for the chemical potential oscillations at $T = 4.2$, $H = 80$ kOe. Although this value is more tham 10^4 times greater than $|\mu_{\mathrm{osc}}|$ for the alkali and precious metals, the anticipated correction $\delta\varphi/2\pi \approx 4\cdot10^{-3}$ to the oscillation phase is still much less than the additional phase shift of the magnetic breakdown oscillations in the resistance and thermal emf observed for beryllium in Ref. 9.

EXPERIMENT

The oscillations in the chemical potential can be observed by measuring the contact potential difference (CPD)[2]. The simplest method is to vary the magnetic field and record the voltage across a measuring capacitor with the sample as one of its plates.[13] A measuring capacitor containing a solid (oxide) dielectric was employed in all of the previous experiments[3–6]; the input impedance of the recording circuit was relatively low ($\sim 10^6$ W), and the measurements were carried out in pulsed magnetic fields.

Because μ_{osc} is expected to be large for beryllium, we anticipated that the chemical potential oscillations might be recorded by an electrometric amplifier in steady magnetic fields. In this case the measurements could be carried out in steady magnetic fields and it was not necessary to oxidize one of the capacitor plates, so that the noise associated with pulsed-field measurements was eliminated.

Figure 1a shows a sketch of the measurement system. The measuring capacitor C was housed in a superconducting solenoid and connected by a coaxial line (coax) to the external head of the electrometer. The head was tightly fastened to the upper end of the coax, which consisted of a stainless steel tube (130 cm long and 15 mm in diameter) containing a stainless steel wire of diameter 0.2 mm stretched between sapphire insulators. The measuring capacitor and the coax formed a capacitive voltage divider. In order to decrease the equivalent capacitance of the coax and enhance the signal reaching the input of the electrometer, we connected the outer tubing of the coax to the output of the electrometer, so that its potential was nearly equal to the potential of the internal wire. The measuring capacitor C discharged across a resistor R mounted at the lower end of the coax.

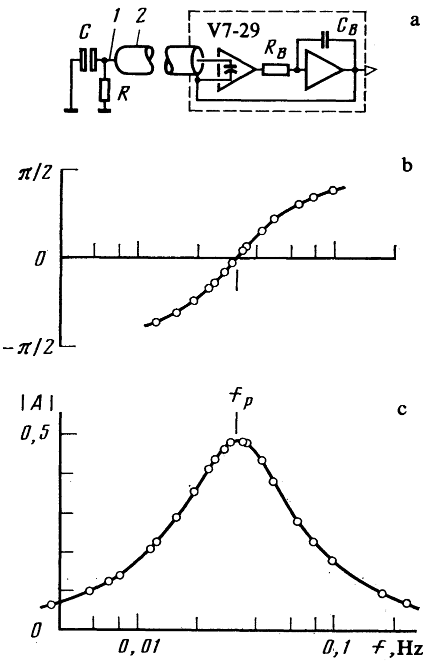

FIG. 1. a) Schematic of measuring device: C, measuring capacitor; 1, 2) coaxial wire and tube; b, c) phase and amplitude transfer characteristics.

The V7-29 electrometer employed a dynamic input capacitor (DC) and operated by the usual principle—the ac voltage from the dynamic capacitor was amplified, synchronously detected, and fed to an integrator, whose output signal compensated the dc voltage across DC. This design ensured a high input impedance (10^{19} Ω) combined with relatively low noise ($20\,\mu$V).

Figure 1 shows that the voltage signal is first differentiated by the R-C circuit and then integrated in the electrometer. The resonance peak in the resultant transfer characteristic of the V7–29 thus makes it easier to detect small oscillations in the chemical potential.

We calibrated the measuring system as follows. The beryllium sample (the left-hand plate of the capacitor in Fig. 1a) was disconnected from the common wire (virtual ground) and connected to an ac voltage of amplitude 3.55 mV supplied by a G3-47 generator. This same voltage signal was fed to the X-coordinate of an X, Y plotter; the Y input was connected to the output of the electrometer. The amplitude-frequency and phase-frequency characteristics of the measuring system were deduced from the ellipses recorded by the plotter. We found the capacitance C from the magnitude of the dc voltage at the electrometer output when a voltage ramp was fed to the capacitor. Figure 1b, c shows some calibration curves for a system with $C = 7.8$ pF and $R = 3.54\cdot10^{11}$ Ω (the KÉV-1 resistor had a nominal resistance of 1 GΩ at room temperature). The integration time constant $R_B C_B$ of the electrometer was equal to 3.3 s.

We tested three measuring capacitor configurations. In the first configuration, a vacuum capacitor was placed inside a molybdenum glass ampul (Fig. 2a). One of the plates of the

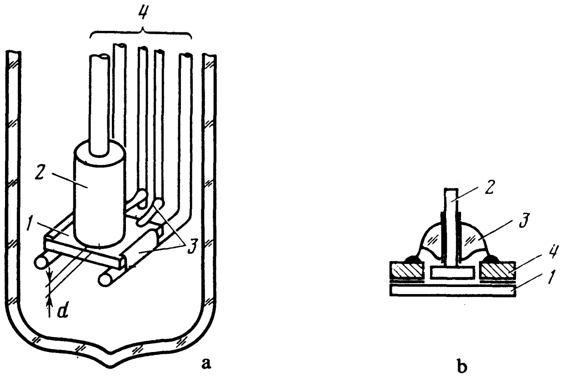

FIG. 2. Two capacitor configurations. a) vacuum capacitor: 1) beryllium sample; 2) Mo electrode; 3) gold foil strip; 4) Mo leads; b) ordinary capacitor: 1) Be sample; 2) bronze electrode; 3) glass insulator; 4) bronze base.

measuring capacitor C consisted of a 0.3-mm-thick Be single-crystal wafer with its [0001] axis normal to the wafer plane (the wafer was secured by gold foil strips to molybdenum leads). A molybdenum electrode of diameter 5 mm served as the other plate. The two plates were separated by $d \approx 0.05$ mm, and the capacitance was 3.5 mF. The ampul was heated to 300 °C and degassed for several days, and the capacitor surfaces were cleaned by ion etching in an argon atmosphere; the ampul was sealed after the internal pressure reached $5 \cdot 10^{-6}$ torr. The Be sample could not be oriented relative to the magnetic field in this system. Measurements of the magnetoresistance of the sample revealed that the hexagonal axis of the crystal made an angle $\alpha \approx 2°$ with the field **H**.

The second design (Fig. 2b) employed a rigid capacitor in which the electrode was soldered into an insulating glass bead. The Be surface was abraded, the damaged layer was etched away in alkaline solution, and the surface was then electrolytically polished. The distance between the capacitor plates (the gap between the electrode and the Be sample) was constant and equal to the width of a roll of thin paper inserted between the plates. The capacitor ($C = 7.8$ pF) was mounted on the rotating platform of the device used in Ref. 9. We used the magnetoresistance signal to orient the sample so that the [0001] direction was exactly parallel to the field **H** (we first rotated the crystal until the signal was a minimum, after which we changed the inclination α until a local maximum was reached).

Finally, the third capacitor was identical to the one shown in Fig. 2b, except that the hexagonal axis of the Be sample lay in the plane of the wafer (we wanted to see how changing the geometry altered the measurement results). In this case, the magnetic field was parallel to the capacitor plates, and the capacitance was equal to 5.2 pF.

The ratio $\rho_{300\,\mathrm{K}}/\rho_{4.2\,\mathrm{K}}$ of the resistances of the Be sample at 300 and 4.2 K was ≈ 380. The magnetic field was measured by a copper sensor calibrated from NMR measurements using a standard ^{27}Al sample.[9]

The measurements were carried out in the following sequence. First we recorded the magnetic breakdown oscillations in the resistance, which were used as a reference background against which the oscillations in the chemical potential could be observed. Since the latter should oscillate at the same frequency as the magnetic breakdown oscillations, the rate f_s at which the magnetic field was swept was chosen to maximize the transfer coefficient of the measuring system (Fig. 1c). The signals from the magnetic field sensor and electrometric amplifier were sampled every 2 s and the results were stored on punched tape. Roughly 200 points were contained in each trace for 75 kOe$\leqslant H \leqslant$80 kOe. The results of 20–30 traces were averaged by computer; during the averaging, the entire range of the magnetic field was divided up into 80 subintervals, each containing roughly 70 points. All of the measurements were made at $T = 4.2$ K.

RESULTS

The experiments using the vacuum measuring capacitor revealed voltage oscillations of amplitude considerably greater than the predicted value μ_{osc} for the chemical potential oscillations. Figure 3 shows some experimental traces. It is noteworthy that the amplitude and phase of the observed oscillations depended on the dc bias voltage applied to the beryllium sample. The trace in Fig. 3a was recorded with the sample connected to the common lead; the oscillation amplitude in this case was 0.74 mV. This increased to 1.6 mV when a bias $E_b = 1$ V was applied, and the oscillation phase was reversed (Fig. 3b). The oscillations could be eliminated by suitably selecting E_b (Fig. 3c).

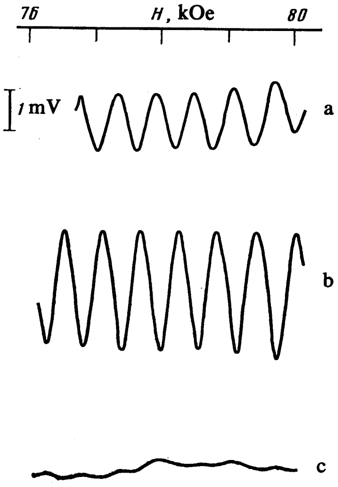

FIG. 3. Voltage traces recorded using the vacuum capacitor; curves a–c) correspond to bias voltage $E_b = 0, -1$, and -0.3 V on the Be sample. The sensitivity of the measuring device was the same for all three traces.

However, these oscillations had nothing to do with oscillations in the chemical potential but were instead associated with the magnetostriction of the Be sample. Indeed, a contact potential difference (CPD) equal to $W_{\mathrm{Mo}} - W_{\mathrm{Be}}$ was present between the Be sample and the Mo electrode (here W_{Be} and W_{Mo} are the respective work functions), and this CPD generated an electric field inside the measuring capacitor (C). The magnetostriction in the Be plate periodically modulated the capacitance (and hence also the charge on C), which was reflected in an oscillating voltage across the resistor R. The field inside C could be changed by varying the bias E_b applied to the Be sample, and the oscillations disappeared completely when E_b canceled the CPD exactly. Our value $W_{\mathrm{Mo}} - W_{\mathrm{Be}} = 0.3$ V for the latter agrees closely with tabulated data.[14]

We can use these measurements to estimate the magnetostriction in the Be sample. The formula $|U_{\mathrm{osc}}| = 2\pi f E R \delta C$ relates the amplitude of the ac voltage across the capacitor to the change δC in the capacitance; here f is the repetition rate of the oscillations. The experimental data imply that $\delta C \approx 3 \cdot 10^{-2}$ pF, which corresponds to a change $\delta d = 4 \cdot 10^{-4}$ mm in the distance between the capacitor plates. If we assume that δd is due entirely to the longitudinal magnetostriction of the sample, we get an implausibly large value $\sim 10^{-3}$ for the magnetostriction coefficient. It seems likely that the clamping of the ends of the Be wafer to the molybdenum lead resulted is distortion (bending) of the wafer due to the transverse magnetostriction; the mechanical amplifi-

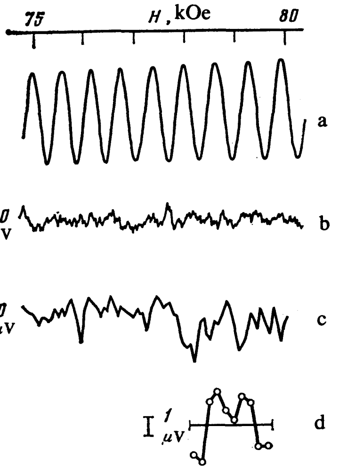

FIG. 4. Traces recorded using the rigid capacitor in Fig. 2b: a) magnetic breakdown oscillations in the resistance of beryllium; b) single voltage trace; c) average of 24 traces; d) result obtained by restricting the averaging procedure in c) to a single oscillation period of the resistance.

cation factor $\sim 10^4$ in this case is quite plausible.

We were able to completely eliminate the magnetostriction voltage oscillations by using the rigid capacitor in Fig. 2b. In this case the ring-shaped insert between the plates kept d constant and no magnetostriction voltage oscillations were detected even for $E_b = 100$ V.

Figure 4 shows the traces measured using the rigid capacitor. For single traces and noise level was too high to permit us to detect chemical potential oscillations of the predicted amplitude $\mu_{\text{osc}} = 17.4\ \mu$V. Substantially better results were obtained by averaging over several traces (Fig. 4b). Nevertheless, we still did not observe any oscillations in the chemical potential, even though the noise level in this case was less than the expected amplitude μ_{osc} (note that the chemical potential oscillations should have the same form as the oscillations in the resistance, cf. Fig. 4a).

We decreased the noise further by averaging the data from multiple traces over a single period of the resistance oscillations. This was done by calculating the phase $\varphi_i = 2\pi\overline{F}/H_i$ of each data point and averaging the corresponding capacitor voltages U_i over time intervals of length $1/\overline{F}$, where $1/\overline{F}$ is the oscillation period. Points whose phases differed by $2\pi(N \pm 0.05)$ for integral N were put in the same averaging interval. No oscillations were detected even after this procedure (Fig. 4d). Numerical analysis revealed that in this case the amplitude of the harmonic of frequency $\overline{F}$ was equal to $1.6\ \mu$V, and the rms deviation of the points from the zero line was $1.5\ \mu$V. The amplitude of the chemical potential oscillations was thus less than the noise amplitude, which indicates that the former was at least an order of magnitude less than expected.

We carried out similar measurements for a Be sample with hexagonal axis inclined at $\alpha = 2°$ relative to the initial orientation $\mathbf{H}\|[0001]$, and for a sample with axis parallel to the wafer surface (third measuring capacitor configuration). Because of the lower capacitance in the latter case, the reduced noise (found by averaging many traces over a single period) was somewhat larger ($2\ \mu$V).

No oscillations in the chemical potential were observed in any of the measurements; more precisely, their amplitude was less than the noise (1.5–$2\ \mu$V), or an order of magnitude less than the expected value μ_{osc}.

DISCUSSION

The prediction of chemical potential oscillations is predicated on the assumption that the electron density per unit volume n_e remains constant in the metal.[1] However, the magnetorestriction causes n_e to vary, and this was neglected in the calculations in Refs. 1 and 2. We stress that the volume changes δV associated with magnetostriction are unavoidable because the latter is thermodynamically equivalent to the pressure dependence of the magnetization.[15,16]

We will confine ourselves to the free electron model in our assessment of the relative contributions from δV and $\delta n(\varepsilon_F)$ to the variations in the chemical potential of metals. In this model, Eq. (1) reduces to

$$\mu_{\text{osc}} = -\frac{2}{3}\frac{\mathbf{M}_{\text{osc}}\mathbf{H}}{N}, \tag{2}$$

where N is the number of electrons.[2]

According to Ref. 16, the volume oscillations δV caused by magnetostriction are also directly proportional to the scalar product $\mathbf{M}_{\text{osc}}\mathbf{H}$, and

$$\delta V/V = -{}^2/_3\beta\mathbf{M}_{\text{osc}}\mathbf{H}, \tag{3}$$

for the free electron model, where β is the compressibility of the metal. Since $\varepsilon_F \sim V^{-2/3}$, δV gives rise to a change

$$\delta\mu/\varepsilon_F = -{}^2/_3\delta V/V \tag{4}$$

in the chemical potential. Equations (3), (4) yield the expression

$$\delta\mu = {}^4/_9\varepsilon_F\beta\mathbf{M}_{\text{osc}}\mathbf{H}$$

for the magnitude of the oscillations in the chemical potential associated with the magnetostriction. If the conduction electrons completely determine the compressibility, then $\beta = 3/2\varepsilon_F N$ and

$$\delta\mu = {}^2/_3\mathbf{M}_{\text{osc}}\mathbf{H}/N. \tag{5}$$

We see by comparing (2) and (5) that the oscillations caused by the variations $\delta n(\varepsilon_F)$ in the density of states completely cancel the magnetostriction-associated changes in the chemical potential in the free electron model, provided the electrons give the dominant contribution to β. This conclusion remains valid regardless of the form of the dispersion law for the electrons; the important thing is that the electrons must completely determine the compressibility of the metal.[17]

The electron contribution to β is generally believed to be just 60–80% (Ref. 18), in which case the magnitude of the chemical potential oscillations given by Eq. (1) should be decreased by a factor of 3–5. Since our experiments indicate a more than tenfold attenuation, the electron contributions to β for beryllium must exceed 90%.

Rigorous calculations lend support to the above conclusion. For example, Table III in Ref. 19 presents calculated results for the lattice and electron contributions to the modulus of compression $B = 1/\beta$ for magnesium; the electron contribution was calculated as an expansion in powers of the electron-ion interaction. These data imply that the ion contribution $B_i = 9.10$ is canceled to within 2% by the sum $B^{(1)} + B^{(2)} + B^{(3)} = 8.92$ of the first-, second-, and third-order terms in the series expansion; the pure electron contribution $B^{(0)} = 3.56$ remains uncanceled, and its magnitude agrees closely with the experimental value $B_{\text{exp}} = 3.69$. (The moduli of compression are given in units of 10^{11} dyn/cm^2.)

The magnetostriction and state density effects thus cancel for beryllium, which explains why no oscillations in the chemical potential were observed in our experiments.

If the above analysis is correct, both the compressibility and the equation of state $P = P(V)$ for beryllium must be determined solely by the conduction electrons. Further experimental work is needed to test this assertion for other metals.

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