

Low-Temperature Compressibilities and Absolute de Haas-van Alphen Frequencies in Potassium, Rubidium, and Cesium

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The absolute de Haas-van Alphen (dH-vA) frequencies and the scaling effect of small hydrostatic pressures on extremal cross sections of the Fermi surface have been measured in freely mounted samples of K, Rb, and Cs. The dH-vA frequencies are in good agreement with those derived from currently accepted values for the low-temperature lattice constants of the three metals at (1.824 ± 0.002) , (1.603 ± 0.003) , and $(1.365 \pm 0.002) \times 10^8$ G, respectively. The low-temperature compressibilities derived from the pressure measurements at $(2.57_7 \pm 0.013)$, $(3.64_4 \pm 0.015)$, and $(4.02_0 \pm 0.02) \times 10^{-2}$ kbar $^{-1}$, respectively, show discrepancies of -5, -8, and -14% with those measured by more conventional techniques. The characteristic energy $B_0 V_0$ (bulk modulus \times atomic volume) is found to be constant at about 1.67×10^5 J/mole in the three metals.

1. INTRODUCTION

Changes in the Fermi surface (F.s.) of a metal as a function of lattice constant may be studied by measuring changes in absolute or relative phase of de Haas-van Alphen (dH-vA) oscillations as a function of hydrostatic pressure in the liquid-helium bath surrounding the sample.^{1,2} Such studies have shown that there are small but measurable *distortions* in the shape of the F.s. in several cubic metals, in addition to the simple scaling effects predictable from the compressibilities of the metals concerned. However, the F.s.'s of the alkali metals potassium (K), rubidium (Rb), and cesium (Cs) differ only slightly from a free-electron sphere,^{3,4} and are thus unlikely to show any appreciable distortion in their shapes under small hydrostatic pressures. On the other hand, since the compressibilities of K, Rb, and Cs are rather large, the *scaling* effect of pressure on their F.s. dimensions will be large and easily measurable. Thus, the low-pressure dH-vA phase shift technique offers a rather precise direct way of measuring what are essentially the *differential* compressibilities of the alkali metals at very low temperatures, using

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pressures that are several orders of magnitude smaller than those used, for example, by Swenson and co-workers,^{5,6} in more conventional investigations of pressure-volume relationships in the alkali metals. Values for low-temperature bulk moduli of the alkali metals may also be derived from elastic constant data obtained by ultrasonic techniques (e.g., by Trivisonno and co-workers⁷⁻⁹), but here again we believe our method is simpler and more precise.

In order to avoid nonhydrostatic effects we have, of necessity, to use freely mounted samples of the alkali metals. This allows us also to determine, with fair precision, the dH-vA frequency corresponding to the extremal cross section of a free-electron sphere in these metals under conditions that have not previously been realized.* Shoenberg and Stiles³ in their study of the F.s.'s of K and Rb, which involved the original use of the dH-vA phase-shift technique in steady high magnetic fields, used single-crystal beads frozen into petroleum jelly in thin-walled glass tubes. Okumura and Templeton,^{4,11,12} in their preliminary measurements on Rb and in their more detailed study of Cs, used single crystals in the form of fine wires crystallized in, and in intimate contact with, thin-walled glass tubes. Both of these techniques, because the thermal contractions of the alkali metals are very much larger than those of either frozen petroleum jelly or glass, could well lead to considerable negative pressures within the single crystals at low temperatures, and thus to erroneously low values of the measured dH-vA frequencies. These effects have been considered by Dugdale and Guban¹³ and also discussed by Shoenberg and Stiles³ and by Okumura and Templeton.⁴ Their absence in the present experiments offers a closer approach to ideal conditions in making an absolute measurement of dH-vA frequency in an alkali metal.

2. THE PRESENT EXPERIMENTS

2.1. The Phase-Shift Method as Applied to the Alkalis

The sensitivity of the dH-vA phase-shift method in measuring changes of an F.s. cross section with pressure is related directly to the area of the cross section concerned and to the compressibility of the material. The smaller sizes of the alkali-metal F.s.'s as compared with those of the noble metals are more than compensated by the much higher compressibilities of the alkalis: The areas in the alkalis are smaller by about 3 times but the compressibilities are larger by about 50 times. The available pressure range of 25 bar at 1 K could then give a precision approaching 0.1%: it is, in fact, possible to detect the effect of as little as 1/40 bar on an alkali-metal sample. This corresponds to a phase shift of about 1/1000 of a dH-vA cycle at 50 kG.

2.2. Equipment and Techniques

The equipment and experimental techniques used have for the most part been described by Templeton.¹ The original pressure bomb and pickup coil were

*Since these measurements were made, we have become aware of the recent high-precision measurements of absolute dH-vA frequency in potassium by Thomas and Turner¹⁰ that were also made on freely mounted samples. See Table I.

used in the 1-in. Westinghouse superconducting solenoid. Measurements of the absolute change of phase of dH-vA oscillations with pressure were made by the null method used in the later measurements on the noble metals. In the case of the alkali metals, of course, there were no problems of spurious phase shift due to intermodulation effects from other extremal cross sections of F.s. The measurements of dH-vA frequency were made with the automatic data recording system and computer processing techniques used by Chollet and Templeton¹⁴ in studying the effect of alloying on the F.s. of copper.

2.3. Specimen Preparation and Handling

Specimen preparation, orientation, and handling were the most delicate parts of the experiment, for which we had to devise or adapt techniques to reach the goal of mounting a clean, undamaged, reasonably well-oriented and oxide-free cylindrical sample in the pressure bomb and of cooling this assembly successfully to liquid-helium temperatures. The difficulties naturally increased markedly as we progressed from potassium to cesium, but, in general, techniques learned for one metal could fairly easily be modified or adapted to suit the next, more active material. The initial procedures for potassium could be carried out under oil in an ordinary atmosphere, but for rubidium and cesium it was found preferable to do most of the handling under oil in a glove box filled with clean, dry helium. We used mineral oil that had been dried with sodium wire and then vacuum-distilled. A stock of this oil, into which fresh potassium wire had been extruded, was kept in a closed flask in the glove box. The glove-box atmosphere, particularly at critical times prior to the exposure of a dry crystal surface, was monitored by cutting slices from a block of potassium and observing the rate of deterioration of the exposed surface. The removal of any traces of moisture diffusing into the box was found to be at least as important as removing oxygen, and a refrigerating coil was used at critical stages to do this. Under the best conditions a cut surface of potassium would remain bright for 15-30 min, while under oil in an open dish the surface would remain bright for a week or more.

The single crystals were required finally to be some 4 mm long and 2 mm in diameter. A selection of glass tubes, each a few inches long and drawn down to have very thin (~ 0.1 mm) walls and an internal diameter of rather over 2 mm, were used as simple moulds to provide the required cylindrical shape. A small phial of high-purity metal was cracked open and placed in a beaker of oil, which was then warmed on a hot plate to just above the appropriate melting temperature. By means of a rubber bulb, several suitably sized beads of molten metal could be drawn (after some practice!) into a sample tube, which was then laid in a shallow dish of cold oil. The inclusion of several beads of metal in each tube provided additional protection to the inner samples against atmospheric corrosion during the x-ray orientation process, which had to be done outside the inert atmosphere of the glove-box. After several tubes of samples had been prepared, the shallow dish of oil in which they lay was warmed gently to some 10°C above the melting point of the metal and was then covered, laid on an insulating pad, and allowed to cool

very slowly. The solidified beads of metal usually showed striations that were apparently related to crystal orientation, so the crystalline uniformity of the various beads could, to some extent, be judged by eye.

Since the experimental samples were to be mounted in a fixed holder with its axis along the magnetic field, only the axial orientation of the crystal, as defined by its cylindrical shape, was of importance. The x-ray determination of this orientation was carried out with the samples still in their original tubes, the ends having been plugged with dry petroleum jelly injected by a hypodermic syringe and finally capped (outside the glove box) with Apiezon Q-compound and a coating of Glyptal cement. The orientation measurement is somewhat complicated in the alkali metals by their rather large interatomic spacing, combined with the very high absorption by both glass and metal of those rather low-energy x rays that can be diffracted through a sufficient angle to give a useful Laue diffraction pattern. However, by using rather thin glass and allowing the x-ray beam to strike only the very edge of the sample, we were able to make reasonably satisfactory transmission Laue pictures.

In preparation for an experiment a tube containing a suitable crystal was returned to the glove box. The coil and pressure bomb had already been introduced via a small hole in the wall of the box and temporarily sealed in place with a split stopper around the beryllium-copper pressure capillary. The glass tube was then carefully cracked and the chosen crystal allowed to slide out into a dish of oil. Then, handled with spatulas of thin card, the specimen was washed in dry xylene and etched gently in xylene containing a little amyl alcohol until, when tried for size under oil, it would just slide into a 2-mm test hole. The etched specimen was finally washed in xylene, allowed to dry briefly, and slid into the pickup coil. The crystal was allowed to rest in position on the base plug of the coil, since it was felt that the light spring normally used would damage the soft metal. The pressure bomb was then screwed into place and the assembly removed from the glove box. The pressure seal was then finally tightened, the external field coils were connected, and the bomb, with a small overpressure of helium gas on the specimen, placed in the cryostat and allowed to cool fairly rapidly to liquid-air temperature. The experimental procedures from that point have already been described.

3. RESULTS AND DISCUSSION

Four specimens of potassium were successfully mounted and run. All gave good signals, but one showed a long beat in the dH-vA oscillations that indicated that this sample was a bicrystal. Rubidium gave good signals from one and fair signals from another of three specimens, while cesium gave good signals in two cases out of seven. Details of the specimens and of the experimental results are given in Tables I and II. In Table III we list our value for the zero temperature bulk modulus B_0 (the reciprocal of the volume compressibility) and the values of atomic volume V_0 corresponding to our values of F_0 , the dH-vA frequency for a free-electron sphere. We compare these with the values given by conventional

TABLE I
Absolute dH-vA Frequencies in 10^8 G

Specimen	F Measured	Orientation correction	F_0	Mean, F_0	Pulsed field, F_0	Lattice const., ^a F_0
K-P1	1.8245	+0.04%	1.8252	1.824 ± 0.002	1.826 ± 0.004 ^a (1.8246 ± 0.0006) ^b	1.832
K-P3	1.8237	-0.04%	1.8230			
K-P4	1.8236	+0.007%	1.8237			
Rb-P1	1.6025 (poor)	-0.23%	1.5988	1.603 ± 0.003	1.601 ± 0.008 ^c	1.603
Rb-P2	1.6036	+0.14%	1.6058			
Cs-P1	1.3589	+0.37%	1.3638	1.365 ± 0.002	1.366 ± 0.003 ^d	1.368
Cs-P2	1.3572	+0.62%	1.3657			

^aOkumura and Templeton (unpublished).

^bThomas and Turner.¹⁰ Measured in a superconducting solenoid with simultaneous NMR calibration.

^cOkumura and Templeton,¹¹ after correction for calibration error (periods to be multiplied by 1.025) and orientation.

^dOkumura and Templeton.⁴

^eBarrett.¹⁷

TABLE II
Compressibilities in 10^{-2} kbar⁻¹

Specimen	Measured $(dA/A)/dP$	Mean "area" compressibility	Equivalent volume compressibility
K-P1	1.722	1.71 ₈ ± 0.008	2.57 ₇ ± 0.013
K-P3	1.721		
K-P4	1.711		
Rb-P1	2.097	2.11 ₀ ± 0.01	3.16 ₄ ± 0.015
Rb-P2	2.110		
Cs-P1	2.691	2.68 ₀ ± 0.013	4.02 ₀ ± 0.02
Cs-P2	2.668		

TABLE III
Atomic Volumes and Bulk Moduli

Material	V_0 (cm ³) (present work)	V_0 (cm ³) (p-v-t, lattice const.)	B_0 (kbar) (present work)	B_0 (kbar) (p-v-t, u-s) ^a	B_0V_0 (× 10 ⁵ J/mole) (present work)	B_0V_0 (× 10 ⁵ J/mole) (p-v-t) ^b
K	43.2 ₄	43.3, 42.96	38.8 ± 0.2	37.0, 36.6	1.68	1.60
Rb	52.4 ₇	53.0, 52.46	31.6 ± 0.15	29, 30.6	1.66	1.54
Cs	66.7 ₅	66.5, 66.52	24.9 ± 0.13	21.5, 23.1	1.66	1.43

^aPressure-volume-temperature, ultrasonic. As quoted by Anderson *et al.*⁶

^bN.B. The p-v-t value of B_0V_0 for Na is 1.68×10^5 J/mole.

high-pressure piston displacement techniques; we also make comparison for B_0 with values derived from ultrasonic measurements of elastic constants and for V_0 with values corresponding to lattice constant data. The values of the product B_0V_0 are also included and compared with the values of this "characteristic energy" from pressure-volume-temperature (p-v-t) measurements as summarized by Anderson *et al.*⁶

The values of F_0 differ very little from those determined by pulsed field measurements, which suggests that "negative pressure" effects, previously put forward as a possible source of anomalously low values of F_0 in enclosed samples, are not in fact important. It is probable, as Shoenberg and Stiles³ suggest, that stresses caused by thermal contraction in the earlier experiments were relieved by plastic flow. The evidence for and against the existence of a "charge density wave" ground state in the alkali metals^{15,16} has been discussed by Thomas and Turner¹⁰ with reference to potassium; the present results certainly offer no support for the theory, which would require that observed values of F_0 should be significantly lower than those calculated from lattice constant measurements. It is now believed that the apparent discrepancy in the case of potassium arises from an error in Barrett's¹⁷ lattice constant figure. The discrepancy corresponds to an error of about -0.2% in lattice constant, which could easily be accounted for by the 0.5% Na in Barrett's potassium.

The comparisons in Table III show that, although there is substantial agreement on the values of V_0 , our values of B_0 appear to be systematically larger than those given by the piston (p-v-t) method. It is perhaps significant that the largest difference is in Cs, where our figure for B_0 is 16% higher, and also perhaps that our values for B_0V_0 in K, Rb, and Cs are essentially equal to the value of 1.68 J/mole given by the p-v-t method for Na. The total pressure range involved in our measurements is 25 bar; we believe our figures to be accurate to better than 0.5% . The p-v-t figures are quoted to 1% ; however, the pressure range involved is 20 kilobar, and indeed the limiting accuracy at low temperatures is about 100 bar. One might query the use of a piston technique in measuring compressibility, since this requires appreciable plastic flow of the compressed metal if its cubic structure is to be maintained. However, the measurements have usually been made on at least two samples of differing length-diameter ratios that should presumably show up any systematic departures from true hydrostatic conditions.

We must conclude then at present that there is a real difference between the differential compressibility (i.e., that measured at essentially constant volume) and compressibility measured under conditions involving appreciable volume change. The fact that the compressibility apparently *increases* with increasing pressure argues a degree of instability in the body-centered cubic structure that is most marked in cesium. Such an instability seems not unlikely since at ~ 22 kbar, after being compressed by some 40% , Cs I transforms to the close-packed cubic Cs II. Though no such transformation occurs in Rb or K, the tendency may well exist, appearing as a departure from linearity in the compressibility.

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