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# The volume dependence of the magnetic susceptibility of the alkali metals

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**Abstract.** The pressure dependence of the total magnetic susceptibility per unit volume, $d\ln\chi_T/dP$, has been measured in the alkali metals at pressures up to 140 MPa, using a SQUID magnetometer. The values obtained for Na, K, Rb and Cs are $0.13 \pm 0.20$, $6.42 \pm 0.95$, $5.46 \pm 0.45$ and $15.59 \pm 0.53$ in units of $10^{-10}$ Pa$^{-1}$, corresponding to values of $d\ln\chi_T/d\ln V$ of $0.10 \pm 0.14$, $-2.46 \pm 0.38$, $-1.71 \pm 0.14$ and $-3.73 \pm 0.14$ respectively.

In Na and K, values of $d\ln\chi_P/d\ln V$ deduced from $d\ln\chi_T/d\ln V$ are discussed in relation to the theory by L Wilk *et al*. Good agreement is found between the experimental and theoretical values, supporting their conclusion that the ion core and crystalline effects must be taken into account in calculations of the spin susceptibility. In Li, for which measurements have not been made in the present work, the theory leads to a rather larger value for the volume dependence of $\chi_P$ than is deduced from CESR work by T Kushida *et al*. There have been no corresponding theoretical calculations for Rb and Cs and the discussion of the values of $d\ln\chi_P/d\ln V$ obtained here is limited to a consideration of relativistic effects and of effects due to the proximity of the 5d band to the Fermi level.

In addition to $d\ln\chi_T/dP$, $\chi_T$ has also been measured for Na, K, Rb and Cs and the resultant volume susceptibilities are: $+7.61 \pm 0.20$, $5.18 \pm 0.19$, $4.24 \pm 0.16$ and $5.36 \pm 0.21 \times 10^{-6}$ SI units respectively. These measurements were made because the values for $\chi_T$ in the literature show a wide spread, and an accurate value is needed for analysis of the data.

## 1. Introduction

The magnetic properties of the alkali metals are frequently studied because of the simplicity of their electronic structure. The Pauli spin susceptibility $\chi_P$ is of particular interest because, though it is strongly dependent on electron–electron interactions, it is not significantly dependent on electron–phonon interactions (Saxena and Bhattacharya 1968). Thus there have been many calculations of $\chi_P$ in jellium which have included the enhancement due to e–e exchange and correlation effects; these have been reviewed by Kushida *et al* (1976, 1979). Agreement between these theories and experiment is reasonable in Na but poor in the other alkalis and particularly so in Li and Cs. The reason for this disparity is that the exchange-correlation enhanced conduction electron spin susceptibility is modified by the core electrons and also by the crystalline effects. A theory due to Vosko and Perdew (1975b) includes these 'real metal' core and crystalline corrections and gives good agreement with experiment.

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The conduction electron densities of the alkali metals lie in the range $3 < r_s < 6$, where $r_s$ is the Wigner–Seitz radius. Most of the calculations lead essentially to the same enhancement of $\chi_P$ in jellium in the range $r_s < 4$, which includes Li ($r_s = 3.25$) and Na (3.93). When corrected for core and crystalline effects this enhancement is also in good agreement with that observed experimentally (Vosko and Perdew 1975a). However, for the low-density regime represented by K (4.86), Rb (5.20) and Cs (5.62), the theories are not in mutual agreement. Some, for example Keiser and Wu (1972), predict saturation of the enhancement of $\chi_P$ at high $r_s$, whereas others, for example Shastry (1978), predict a continuing increase of $\chi_P$ with increasing $r_s$. Macdonald and Vosko (1976) have compared the Keiser and Wu and the Shastry theories after allowing for both the core and the crystalline effects using the theory of Vosko and Perdew (1975b). The Keiser and Wu approach leads to good agreement with the experimental values in Li, Na, K and Rb but to a slight over-estimate in Cs; the Shastry approach leads to good agreement in Li and Na, a considerable over-estimate in K and Rb and to a very serious over-estimate in Cs.

In Na, the calculated value of $\chi_P$ in jellium is in reasonable agreement with experiment even without the 'real metal' corrections, whereas its calculated volume dependence (Wilk *et al* 1979) is in very poor agreement with experiment unless these corrections are applied. The volume dependence of $\chi_P$ thus depends more critically on the XC terms than $\chi_P$ and so provides a more incisive way of investigating these effects.

In this work, we have measured the pressure dependence of $\chi_T$ for the alkali metals Na, K, Rb and Cs. There have been no such previous measurements for these elements and the results are of interest in their own right. From $\mathrm{d}\ln\chi_T/\mathrm{d}P$ we have deduced $\mathrm{d}\ln\chi_T/\mathrm{d}\ln V$ and expressed this in terms of $\mathrm{d}\ln\chi_P/\mathrm{d}\ln V$, $\mathrm{d}\ln\chi_L/\mathrm{d}\ln V$ and $\mathrm{d}\ln\chi_I/\mathrm{d}\ln V$ and so obtained values of $\mathrm{d}\ln\chi_P/\mathrm{d}\ln V$, which have been compared with values calculated by Wilk *et al* (1979) in Li, Na and K. (Here $\chi_L$ and $\chi_I$ are the Landau–Peierls and ion core susceptibilities respectively). In Rb and Cs, no theoretical estimates of $\mathrm{d}\ln\chi_P/\mathrm{d}\ln V$ have been made and the present values for these metals are discussed briefly in terms of relativistic effects and possible contributions arising from the proximity of the 5d band to the Fermi level.

## 2. Experimental details

### 2.1. SQUID magnetometer

The volume susceptibility was measured, using a SQUID magnetometer, by passing the sample of the alkali metal, contained within a CuBe pressure vessel, through a pair of pick up coils, wound in the gradiometer configuration to minimise pick-up. To allow for the magnetic properties of the pressure vessel, two sets of measurements were made: the first was of the signal from the vessel and sample, and the second was of the signal from the empty vessel. The signal due to the sample was obtained by subtraction of these two signals. The CuBe was a special binary alloy, without ferromagnetic binders, supplied by the Cabot Corp.

The measurements of the pressure dependence of the susceptibility were made at $\sim 150$ K, using He gas as the pressure medium. At this temperature the cryostat of the SQUID magnetometer was at its most efficient and the chemical reactivity of the metals was greatly inhibited. In the measurements, $\sim 200$ cycles with the sample in position in the pressure vessel were made at each pressure and an average taken; similarly $\sim 1000$

cycles were made with the empty sample holder at zero pressure. (After allowing for the contribution due to the He gas, the signal from the CuBe sample holder did not change significantly with pressure.) The measuring process, which is entirely executed under computer control, takes ~2 min per cycle and the duration of the measurement at each pressure is thus ~12 h. One complete set of measurements takes ~1 month and during this time the liquid He level in the cryostat was maintained between closely defined limits; this was to avoid changes in the magnetic field which would occur if the superconducting shields in the cryostat or the magnet were allowed to become normal. These precautions ensured that precisely the same magnetic field was maintained throughout the entire period.

Checks were made in preliminary work on other metals to verify that the subtraction of the SQUID signal obtained with the pressure vessel empty from the signal obtained with the sample in the pressure vessel gave a result which was proportional to the volume susceptibility of the metal. In addition, the adequacy of the He gas correction was assessed from pressure measurements on a relatively incompressible metal, tungsten.

At the maximum pressure used of 140 MPa, the changes in density in Na, K, Rb and Cs are ≃1.2, 3.5, 4.5 and 6.0% respectively. It is because these changes are so small, coupled with the weak volume dependence of these metals, that a highly sensitive magnetometer was needed for the measurements of the volume dependence of the susceptibility†. The equipment has been described in detail in an earlier publication (Rowley and Myers 1986).

## 2.2. Pressure equipment

The pressure medium was He gas, ensuring hydrostatic conditions. Pressures up to 140 MPa were produced using a Pressure Products two-stage compressor and He gas of 99.995% purity supplied by BOC Special Gases. Because He has a significant susceptibility at high pressure, a correction was made as discussed below; also gas of the highest purity available was used.

## 2.3. Gouy balance

The Gouy balance was based on an electromagnet capable of producing a magnetic field of 1 T and an Oertling balance capable of measuring 1 $\mu$g. The samples were uniform cylinders of ~6 mm diameter and length 250–300 mm contained in evacuated glass tubes; the contribution from the glass was obtained from measurements on an identical empty tube made from the same length of tubing. These measurements were quite conventional and will not be discussed further.

## 2.4. Sample preparation

The samples were made from ampoules having a nominal weight of 5 g. The Rb was supplied by Metals Research Ltd and all other metals were supplied by Koch-Light Ltd. The purities were specified as: greater than 99.95% for Na, 99.97% for Rb and K and 99.98% for Cs; most of the impurities are other alkalis. The very weak susceptibilities

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† Probably a better term instead of the volume dependence of the susceptibility is the density dependence of the susceptibility. The former, however, is in common usage in the literature and for this reason it is retained here.
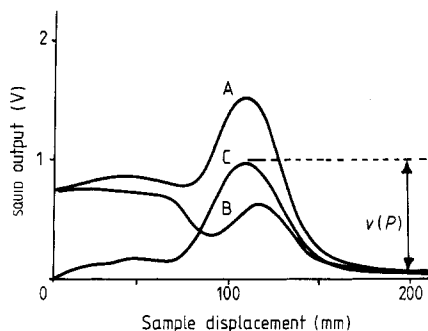
**Figure 1.** Plot of SQUID output voltage as a function of sample displacement. Curve A, sample holder and sample; curve B, empty sample holder; curve C, $v(P)$ is the difference between curves A and B.

of these metals and the comparatively high susceptibility of their oxides necessitates very careful preparation and handling of the samples. In addition, great care was taken to ensure that the pressure vessel was free from contamination at all times.

The Na and K samples were prepared by first melting the metal into a die under high vacuum and them extruding it under cool paraffin oil, which had been dried by extended contact with K metal, to form cylinders of $\sim$6 mm diameter. Because of their reactivity, the Rb and Cs samples were cast directly into the pressure vessel under high vacuum conditions, so forming a cylinder of diameter 7.05 mm. Great care was taken with all the samples to ensure that uniform, voidless samples were produced.

## 3. Analysis

A typical plot of the SQUID output voltage versus sample position is shown in figure 1 for the full and empty sample holder. The voltage $v(P)$ is obtained by subtraction of these two voltages at each pressure $P$. $v(0)$, the difference at zero pressure, is proportional to the volume susceptibility at zero pressure, is proportional to the volume susceptibility of the sample and its cross-sectional area (see for example Cukaukas *et al* 1974). However, at other pressures a correction is necessary for the susceptibility of the He gas in the pressure vessel. This correction is made after calculating at each pressure the effective cross-sectional area of the He, i.e. the difference in areas between the sample and the pressure vessel. To do this the isothermal bulk modulus data for the alkalis of Anderson and Swenson (1983, 1985) and similar data for the CuBe supplied by Cabot Corp. were used. The susceptibility of the gas at the temperature and pressure employed are needed to make this correction, and to obtain this the molar volume under these conditions is required together with the mass susceptibility of He at normal temperature and pressure. Following Rowley and Myers (1987), it was assumed that the mass susceptibility was independent of temperature and had only a small volume dependence; this last assumption is supported by the small volume dependence of the DC electric polarisability as calculated by Ten Seldam and De Groot (1952), which may be related to the volume dependence of the diamagnetic susceptibility of the closed-shell electronic structure of He gas.

In addition to the above correction, it is necessary to correct for the variation of the area of the sample with pressure and temperature. Again, the isothermal bulk modulus data of Anderson and Swenson (1983, 1985) was used to do this.

**Table 1.** Total magnetic volume susceptibility $\chi_T$ ($10^{-6}$ SI units).

| Li | Na | K | Rb | Cs | Reference |
|---|---|---|---|---|---|
| — | 7.61 ± 0.20 | 5.18 ± 0.19 | 4.24 ± 0.16 | 5.36 ± 0.21 | This work, (G) |
| | | 5.33 ± 0.21 | | | Rowley (1986) (G) |
| 23.1 ± 0.5 | — | — | — | — | Leuken (1978) (F) |
| 22.5 ± 0.8 | 7.42 ± 0.18 | 4.88 ± 0.39 | 4.24 ± 0.20† | 4.91 ± 0.45 | Collings (1965) (C) |
| — | 7.2 | 5.0 | — | — | Venkataswarlu and Sriraman (1958) (C) |
| — | 8.5 ± 0.4 | — | — | — | Bowers (1955) (G) |
| — | 8.25 | 5.39 | 4.33 | 5.37 | Bohm and Klemm (1939) (G) |
| 22.9 ± 0.3 | 7.69 ± 0.22 | 5.18 ± 0.10 | 4.26 ± 0.10 | 5.25 ± 0.14 | 'Best value' |

The measurements were taken at temperatures in the range 293–303 K. C, Curie Method; F, Faraday Method; G, Gouy Method. † uncertainty estimated from significant figures quoted.

After allowing, as described above, for the He and area corrections, the resultant output voltage $v'(P)$ is directly proportional to $\chi_T(P)$ at each pressure. The pressure dependence of the susceptibility, d ln $\chi_T$/d$P$, is then obtained from a least-squares fit to a plot of $\chi_T(P)/\chi_T(0)$ against $P$. Here $\chi_T(P)/\chi_T(0)$ is obtained by extrapolating the plot of $v'(P)$ against $P$ to zero pressure to give $v'(0)$ and then putting $v'(P)/v'(0) = \chi_T(P)/\chi_T(0)$. The volume dependence is obtained by using the bulk modulus data of Anderson and Swenson (1983, 1985) to determine $V(P)/V(0)$ at each pressure; d ln $\chi_T$/d ln $V$ is then obtained from a least-squares plot of $\chi_T(P)/\chi_T(0)$ against $V(P)/V(0)$.

## 4. Results

The values of $\chi_T$, measured in this work using the Gouy method, are given in table 1 together with those of other workers; a 'best value' obtained by taking an average of all the data, weighted by the quoted uncertainties, is also given.

Plots of $\chi_T(P)/\chi_T(0)$ against $P$ are shown in figure 2; the plots of $\chi_T(P)/\chi_T(0)$ against $V(P)/V(0)$ are very similar, though here the measurements at each pressure must be first corrected as explained in § 3. The values of d ln $\chi_T$/d ln $V$ obtained for Na, K, Rb and Cs from the least-squares gradient are given in table 2, together with their associated errors. Values of d ln $\chi_T$/d ln $V$ can be deduced from measurements of the temperature dependence of the magnetic susceptibility and this has been done using the data of Bowers (1955) for Na and Collings (1965) for Na, K, Rb and Cs. It was assumed in doing this that the mass susceptibility is independent of temperature. These values of d ln $\chi_T$/d ln $V$, also given in table 2, are in agreement with the present work, within the experimental errors, in the cases of Na, Rb and Cs. In K, however, they are in very poor
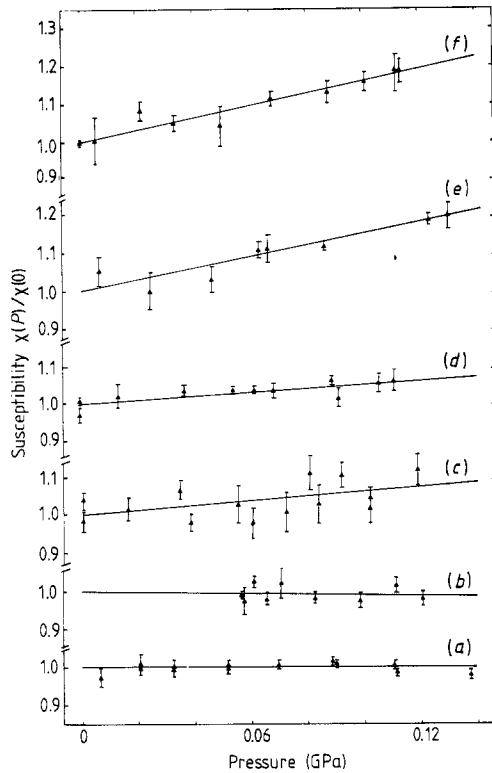
**Figure 2.** Plots of $\chi(P)/\chi(0)$ against pressure for: (a) Na, sample 1; (b) Na, sample 2; (c) K; (d) Rb; (e) Cs, sample 1; (f) Cs, sample 2.

**Table 2.** Pressure and volume dependence of the total magnetic volume susceptibility.

|  | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| $\mathrm{d}\ln\chi_T/\mathrm{d}P$ $(10^{-10}\,\mathrm{Pa}^{-1})$ | —† | $-0.13 \pm 0.20$‡ | $6.42 \pm 0.95$§ | $5.46 \pm 0.45$ | $15.59 \pm 0.53$‡ |
| $\mathrm{d}\ln\chi_T/\mathrm{d}\ln V$ | — | $+0.10$‡ | $-2.14$§ | $-1.71$‡ $(\pm 0.14)$ | $-3.73$‡ |
|  | $-1.4 \pm 0.4\|$ | $+0.1 \pm 0.4\|$ | $-1.0 \pm 0.2\|$ | $-1.5 \pm 0.1\|$ | $-3.5 \pm 0.2\|$ |
|  | — | $0.0$¶ | — | — | — |
|  | $-1.2$†† | — | — | — | — |

† Not measured.
‡ Present work, two sets of data for Na and Cs, one for Rb.
§ Average of present work with that of Rowley (1986); $\mathrm{d}\ln\chi_T/\mathrm{d}\ln V$ for present work, $-2.46 \pm 0.38$; for Rowley, $-1.9 \pm 0.4$.
$\|$ From temperature dependence of $\chi_T$ (Collings 1965).
¶ From temperature dependence of $\chi_T$ (Bowers 1955).
†† From temperature dependence of $\chi_T$ (Leuken 1978).

agreement. An independent measurement of $\mathrm{d}\ln\chi_T/\mathrm{d}\ln V$ in K, however, is in agreement with the present work (Rowley 1986); this is included in table 2. The present measurements were made at a temperature of $\sim$150 K while those of Bowers were taken over the range 55 K to 293 K; the measurements of Collings consisted of two measurements, one at 78 K and one at 298 K. Hence the values can only be compared

if the mass susceptibility has a weak temperature dependence or none at all. Despite the disagreement in K, there is good overall agreement, confirming that the temperature dependence of the mass susceptibility is very small.

SQUID measurements were not made on Li and the value for $d\ln \chi_T/d\ln V$ shown in table 2 was obtained from the work of Collings (1965) and Leuken (1978) on the temperature dependence of $\chi_T$.

The susceptibility $\chi_T$ in the alkalis is usually written as

$$\chi_T = \chi_P + \chi_L + \chi_I. \tag{1}$$

From equation (1) it may be shown that

$$\chi_T \, d\ln \chi_T/d\ln V = \chi_P \, d\ln \chi_P/d\ln V + \chi_L \, d\ln \chi_L/d\ln V + \chi_I \, d\ln \chi_I/d\ln V. \tag{2}$$

To obtain $d\ln \chi_P/d\ln V$ from equation (2) values of $\chi_T$, $\chi_P \, d\ln \chi_T/d\ln V$, $\chi_I$, $d\ln \chi_I/d\ln V$, $\chi_L$ and $d\ln \chi_L/d\ln V$ are needed.

$\chi_T$ has been measured for Na, K, Rb and Cs in the present work and a best value has been obtained as already discussed. $\chi_P$ is taken as an averge of the following measurements, weighted as before: Hecht (1963), Kettler *et al* (1969), Kushida *et al* (1976) and Whiting *et al* (1978) for Li; Schumacher and Vehse (1963), Dunifer (1974), Kushida *et al* (1976), Perz and Shoenberg (1976), Whiting *et al* (1978) and Mace *et al* (1984) for Na; Dunifer (1974), Knecht (1975) and Mace *et al* (1984) for K; Knecht (1975) for Rb; Knecht (1975) and Springford *et al* (1983) for Cs. $\chi_I$ for all the alkalis is taken to have the value recommended on the basis of experimental and theoretical work by Myers (1952). These values of $\chi_T$, $\chi_P$ and $\chi_I$ are given in tables 1, 3 and 4. $\chi_L$ is not directly accessible experimentally but can be deduced from equation (1) using the above values of $\chi_T$, $\chi_P$ and $\chi_I$. The values of $\chi_L$ obtained are given in table 5 together with theoretical estimates.

The present values of $d\ln \chi_T/d\ln V$ are taken, except in K where a weighted average of the present work and the results of Rowley (1986) is used (see table 2). The ionic mass susceptibility is assumed not to vary with volume, from which it follows that $d\ln \chi_I/d\ln V = -1$. $d\ln \chi_I/d\ln V$, like $\chi_L$, is not experimentally accessible but since the values of $\chi_L$ shown in table 5 are very close to the free electron result, the free electron volume dependence for $\chi_L$ will be assumed.

One further problem remains: the averaged value of $\chi_P$ discussed above is a low-temperature result, obtained at ~4 K. It is necessary to adjust this to its equivalent value at ~150 K and, because $d\ln \chi_P/d\ln V$ is needed to do this, $d\ln \chi_P/d\ln V$ itself can only be obtained by iteration. In this the following volume dependences are assumed initially: for Li and Na the results of Kushida *et al* (1976); for K a weighted average of the results of Kushida *et al* (1979) and Chotalia (1988); for Rb and Cs, in the absence of any experimental or theoretical work, the free electron result. An alternative starting point in the case of Rb and Cs, based on the value of $\chi_P$ at 4 K, leads to virtually the same results. The various terms discussed above are now used in equation (2) to deduce a value of $d\ln \chi_P/d\ln V$. This is used to re-calculate $\chi_P$ at 150 K from its low-temperature value. The value of $d\ln \chi_P/d\ln V$ is then re-calculated using equation (2) and the iteration is repeated until there is no change in its value to four significant figures. The values of $d\ln \chi_P/d\ln V$ so obtained are given in table 6. In the case of Rb and Cs, there is considerable theoretical input, but nevertheless these values are the first volume dependences of $\chi_P$ with any experiment input.

The resultant value of $d\ln \chi_P/d\ln V$ for Na agrees, within the experimental errors, with the result of Kushida *et al* (1976), and both are close to the free electron result of

**Table 3.** Pauli spin susceptibility $\chi_P$ ($10^{-6}$ SI units). Experimental values at various temperatures and using various techniques: CESR (C), Knight shift (K), spin wave (sw) and de Haas–van Alphen (DHVA).

| Li | Na | K | Rb | Cs | Reference |
|---|---|---|---|---|---|
| 26.1 ± 1.3 (300 K) | 11.9 ± 1.3 (79 K) | — | — | — | Schumacher and Slichter (1956) (C) |
| — | 14.2 ± 0.6 (293 K) | — | — | — | Schumacher and Vehse (1963) (C) |
| 24.6 ± 1.3 (300 K) | — | — | — | — | Hecht (1963) (C) |
| — | — | 10.6 ± 1.0 (room temperature) | 10.1 ± 1.0 (room temperature) | 10.1 ± 1.0 (room temperature) | Kaeck (1968) (K) |
| 26.3, 27.4 (298 K), (4.2 K) | 13.1 ± 0.9 (5 K) | — | — | — | Kettler et al (1969) (C) |
| — | — | 11.5 ± 0.8 (5 K) | — | — | Dunifer (1974) (sw) |
| — | — | 11.59 ± 0.04 (1.2 K DHVA) | 11.00 ± 0.06 | (10.40 or 13.24) ±0.35 | Knecht (1975) |
| 24.9 ± 0.5 (Room temperature) | 13.4 ± 0.5 | — | — | — | Kushida et al (1976) (C) |
| — | 13.73 ± 0.06 (2 K, DHVA) | — | — | — | Perz and Shoenberg (1976) |
| 27.21 ± 0.49 (295 K) | 13.44 ± 0.15 (77 K) | — | — | — | Whiting et al (1978) (C) |
| 28.5 ± 7.0 (293 K) | 19.7 ± 5.6 (293 K) | — | — | — | Witt and VanderVen (1979) (C) |
| — | — | — | — | 12.65 ± 0.06 (2 K, DHVA) | Springford et al (1983) |
| — | 13.54 (5 K) | 11.66 ± 0.13 (5 K) | — | — | Mace et al (1984) (sw) |
| 27.4 ± 0.1† | 13.63 ± 0.14 | 11.60 ± 0.03 | 11.00 ± 0.06 | 12.73 ± 0.06 | 'Best value' at 4.2 K |
| 15.9 ± 0.6 | 13.79 ± 0.38 | — | — | — | 'Best value' at 293 K |

† Assumed uncertainty—taken from quoted significant figures.

**Table 4.** 'Best values' for the ion core susceptibility $\chi_1$ ($10^{-6}$ SI units). (Myers 1952).

| Li | Na | K | Rb | Cs |
|---|---|---|---|---|
| $-1.16$ | $-2.70$ | $-3.61$ | $-4.58$ | $-6.58$ |

**Table 5.** Landau–Peierls volume susceptibility $\chi_L$ ($10^{-6}$ SI units).

| Li | Na | K | Rb | Cs | Reference etc |
|---|---|---|---|---|---|
| 3.34 | 2.76 | 2.23 | 2.09 | 1.93 | Free electron result |
| 3.50 | 2.84 | 2.22 | 2.06 | 1.87 | Fletcher and Larson (1958) (exchange and correlation) |
| 2.93 | 2.61 | 2.21 | 1.99 | 1.82 | Misra and Roth (1969) (pseudopotential) |
| 1.88 | 2.95 | 3.03 | 3.13 | 3.13 | Isihara and Tsai (1971) (grand partition function) |
| 2.05 | 2.86 | 2.24 | 1.96 | 1.38 | Isihara and Kojima (1975) (grand partition function) |
| —— | 2.56 | 2.29 | 2.27 | 2.21 | Lai *et al* 1978 (pseudopotential) |
| 2.72 | 3.56 | 3.00 | 2.73 | 2.18 | Kojima and Isihara (1979) (grand partition function) |
| $3.1 \pm 0.9$ | $3.0 \pm 0.4$ | $2.6 \pm 0.2$ | $2.0 \pm 0.2$ | $0.6 \pm 0.2$ | Present work |

**Table 6.** Volume dependence of the Pauli susceptibility $\mathrm{d}\ln \chi_P/\mathrm{d}\ln V$ ($10^{-6}$ SI units). Experimental values deduced from measurements at a variety of temperatures and using various techniques: CESR (C); de Haas–van Alphen (DHVA); and SQUID magnetometer (S).

| Li | Na | K | Rb | Cs | Reference |
|---|---|---|---|---|---|
| — | $-0.47 \pm 0.1$ | $-1.39 \pm 0.2$ | $-1.17 \pm 0.25$ | $-2.19 \pm 0.4$ | Present work |
| | | (All work at 150 K, Pressure < 140 MPa) | | | |
| — | — | $-1.3 \pm 0.2$ | — | — | Rowley (1986) |
| | | (187 K, <140 MPa) | | | SQUID Magnetometer |
| — | — | $-1.19 \pm 0.28$ | — | — | Chotalia (1988) |
| | | (2 K, <70 MPa) | | | de Haas–van Alphen |
| $-1.3 \pm 0.1$ | $-0.34 \pm 0.03$ | — | — | — | Kushida *et al* (1976) |
| (4.2 K) | (4.2 K) | | | | CESR |
| — | — | $-0.9 \pm 0.1$ | — | — | Kushida *et al* (1979) |
| | | (4.2 K, <140 MPa) | | | CESR |
| — | — | $-0.7 \pm 0.1$ | — | — | Kushida *et al* (1979) |
| | | (4.2 K, <550 MPa) | | | CESR |

$\mathrm{d}\ln \chi_P/\mathrm{d}\ln V = -\frac{1}{3}$. For K the result is rather higher than that due to Kushida *et al* (1979), but is in agreement within the errors with Chotalia (1988). The maximum pressure used by Kushida *et al* was 550 MPa, however, compared with a maximum of 140 MPa in this work and 70 MPa by Chotalia (1988). Calculations by Wilk *et al* (1979), predict that non-linearity in the volume dependence of $\chi_P$ sets in for $V(P)/V(0) \leqslant 0.9$. The maximum pressure used by Kushida *et al* (1979) produces a compressed volume of 0.87 and their

results are therefore also presented in table 6 for pressures up to 140 MPa; this yields a pressure dependence in closer agreement with that obtained in the present work.

The values of $\mathrm{d}\ln \chi_P/\mathrm{d}\ln V$ obtained here for Rb and Cs are the first to have been determined by any means. The value in Rb is of similar magnitude to that in K but it is particularly interesting that the value for Cs is considerably larger.

## 5. Discussion

The only theoretical work taking into account the crystalline and core effects is the variational theory due to Vosko and Perdew (1975a). Wilk *et al* (1979) have used their results to calculate the volume dependence of $\chi_P$ for Li, Na and K. The theory expresses $\chi_P$ in terms of the single-particle density of states mass $m_s$ at the auxiliary Fermi surface and a complex integral $I$ which is a measure of the reduction in energy due to exchange and correlation when a magnetic field is applied; the expression for the ratio of the spin susceptibility to its free electron value $\chi_P^f$ is

$$\chi_P/\chi_P^f = (m_s/m)/[1 - (m_s/m)I].$$  (3)

$I$ includes: $\gamma(r)$, a quantity proportional to the single-particle magnetisation density; the electron number density $n(r)$; the magnetisation density $m$ and the spin susceptibility in a homogeneous gas of interacting electrons $\chi_h$. $r$ is a position coordinate. Rasolt and Vosko (1974) have emphasised that the real and auxiliary surfaces are not necessarily equivalent, though in practice the two are approximately the same (Wilk *et al* 1979). The volume dependence of $\chi_P$ has been obtained from equation (3) with the volume dependences of $m_s/m$ and $I$ given by Wilk *et al* (1979) as

$$(m_s/m)_v = (m_s/m)_0 + b\Delta r_s + o(\Delta r_s)^2$$  (4)

and

$$I_v = I_0 + a\Delta r_s$$  (5)

Here the superscripts $v$ and 0 indicate the compressed and uncompressed cases respectively, and $\Delta r_s$ is the change in the radius parameter upon compression, which has been calculated in the present work using the bulk modulus data of Anderson and Swenson (1983, 1985). The constants $a$, $b$ and $c$ have been calculated by Wilk *et al* for Li, Na and K, two values for $a$ being calculated corresponding to the Keiser and Wu and the Shastry theories. From equations (4) and (5), it may be shown that the volume dependence is given by

$$\mathrm{d}\ln(m_s/m)/\mathrm{d}\ln V = r_s(b + 2c\,\Delta r_s)/3(m_s/m)$$  (6)

$$\mathrm{d}\ln I/\mathrm{d}\ln V = ar_s/3I.$$  (7)

The various parameters discussed above, including $\mathrm{d}\ln \chi_P/\mathrm{d}\ln V$, have been calculated for a pressure of 140 MPa and the results for Li, Na and K are given in table 7. For Li, the Keiser and Wu and the Shastry theories agree with one another well and both agree fairly well with the experimental values of $\mathrm{d}\ln X_P/\mathrm{d}\ln V$. Since we have already observed that the volume dependence of $\chi_P$ is especially sensitive to the crystalline effects, the slight disparity could be due to an inadequate allowance for them. For Na, the two theories are in good agreement with experiment. For K the agreement is excellent with Keiser and Wu, whereas with Shastry there is a marked over-estimate, adding further support for the former theory in the low-density regime.

**Table 7.** Calculation of $\chi_P$ and dln $\chi_P$/dln $V$ at 140 MPa for Li, Na and K following Wilk *et al* (1979).

|  | Li | | Na | | K | |
|---|---|---|---|---|---|---|
|  | S | KW | S | KW | S | KW |
| $a$ | 0.08380 | 0.06480 | 0.07044 | 0.04139 | 0.06254 | 0.02460 |
| $I_0$ | 0.3249 | 0.3016 | 0.3659 | 0.3278 | 0.3936 | 0.3319 |
| $I_v$ | 0.3239 | 0.3008 | 0.3641 | 0.3268 | 0.3900 | 0.3305 |
| $\chi_P/\chi_s$ | 1.9976 | 1.8649 | 1.6027 | 1.5095 | 1.7460 | 1.5676 |
| $(\chi_P/\chi_P^f)_v$ | 3.0801 | 2.8755 | 1.6553 | 1.5590 | 1.9127 | 1.7173 |
| $(\chi_P/\chi_P^f)_0$ | 3.0622 | 2.8582 | 1.6555 | 1.5573 | 1.8968 | 1.6981 |
| dln $I$/dln $V$ | 0.2806 | 0.2337 | 0.2558 | 0.1675 | 0.2579 | 0.1197 |
| dln$(\chi_P/\chi_s)$/dln $V$ | −0.1276 | −0.1514 | 0.0981 | 0.0380 | 0.0034 | −0.0758 |
| dln $\chi_P$/dln $V$ | −0.8698 | −0.8934 | −0.3282 | −0.3883 | −0.5832 | −0.6624 |
| (dln $\chi_P$/dln $V$)$_{exp}$ | −1.3 ± 0.1† | | −0.47 ± 0.1‡ | | −1.39 ± 0.2‡ | |
| $b$ | −0.5810 | | −0.07262 | | −0.1585 | |
| $c$ | 0 | | 0 | | 0.1220 | |
| $(m_s/m)_0$ | 1.535 | | 1.031 | | 1.086 | |
| $(m_s/m)$ | 1.542 | | 1.033 | | 1.096 | |
| dln$(m_s/m)_0$/dln $V$ | −0.4087 | | −0.0930 | | −0.2533 | |
| $\Delta rS$ | −0.0118 | | −0.0249 | | −0.0575 | |
| $V_P$ | 0.9892 | | 0.9814 | | 0.9651 | |

† Kushida *et al* (1976) at 293 K.
‡ Present work at 150 K.
S, Shastry (1978). KW, Keiser and Wu (1972).

It may be shown from equation (3) that the volume dependence of $\chi_P$ can be expressed as

$$\text{dln } \chi_P/\text{dln } V = \text{dln } \chi_P^f/\text{dln } V + [\text{dln}(m_s/m)/\text{dln } V][1 + I(\chi_P/\chi_P^f)]$$
$$+ (\text{dln } I/\text{dln } V)[I(\chi_P/\chi_P^f)] \tag{8}$$

i.e. as the volume dependence of the free electron susceptibility plus two other terms, one of which includes the volume dependence of $m_s/m$ and the other includes the volume dependence of $I$. These two additional terms represent the departure from the free electron volume dependence of $\chi_P$. For Li and K the volume dependence of the XC enhancement term, dln $I$/dln $V$, is weak in comparison to dln $(m_s/m)$/dln $V$, which is therefore largely responsible for the departure from free electron behaviour. For Na, the situation is different because, though dln $I$/dln $V$ is similar in magnitude in Li, K and Na, the opposing term dln $(m_s/m)$/dln $V$ is much weaker here, leading to only a very small departure from free electron behaviour. Thus, the strong volume dependence in Li and K is due to the strong volume dependence of the crystalline effects, while the weak dependence of this in Na, together with the weak and opposing enhancement term, leads to approximately the free electron result in this metal. A similar analysis of the experimental results to the above was given by Wilk *et al* (1979) but based on the data then existing.

dln $\chi_P$/dln $V$ in Rb is similar in magnitude to the value in K; this might be expected since the metals are similar in other respects, for example in the value of $\chi_P/\chi_P^f$; in addition, the relativistic effects are small in both metals (Macdonald and Vosko 1976). The situation is quite different in Cs which has a much larger value of dln $\chi_P$/dln $V$ and, as shown by Macdonald and Vosko, in which relativistic effects are much greater. It is

likely that the proximity of the 5d band to the Fermi level is important here. Yamashita and Asano (1970) have calculated the band structure at various pressures and they predict an increase in the amount of charge in the d states together with an accompanying decrease in the charge in the s and p states as the volume is reduced. This would result in a sharply increasing d like character of the electrons, increasing localisation of the conduction electrons at the lattice sites and hence increasing paramagnetism. It therefore seems likely that the large volume dependence of the Pauli spin susceptibility in Cs is partly due to this effect. This is rather speculative, however, pointing clearly to the need for calculations of $d\ln \chi / d\ln V$ for Rb and Cs. Measurement of $d\ln \chi_P / dn V$ in Cs, perhaps using the Chotalia method, would also help to clarify the situation.

## 6. Conclusions

Direct measurements of the volume dependence of the total magnetic susceptibility have been made for the first time in Na, K, Rb and Cs. The calculations of Wilk *et al* (1979), which include crystalline and core effects, have been shown to give results in agreement with the experimental values for the volume dependence of the total magnetic susceptibility in Li, Na and K. The interpretation of the volume dependence of Rb and Cs is more complicated than in the other metals, particularly because of the need to undertake relativistic calculations, which are especially important in Cs. There is also need for further experimental work in Rb and Cs on the volume dependence of the spin susceptibility, which might have to be along the lines of Chotalia's de Haas–van Alphen work in K, remembering that the CESR method is unable to cope with the heavier elements (Kushida *et al* 1979).

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