Gewicht fällt einiges für sich, andererseits ermöglicht die B 1-Korrelation eine Anpassung der Rumpfelektronen an die äußere Korrelation zu einer B 2-Gesamtkorrelation. –

Die Deutung des „anomalen" Kristallgitters des Zinks ist seit der Strukturbestimmung von HULL und DAVEY [19] versucht worden an Hand mannigfacher Argumente: Elliptische Gestalt der Atome [20], $(8\text{-}N)$-Regel, d. h. homöopolare Bindungskräfte [21], BRILLOUIN-Zoneneinfluß [22], Einfluß eines nur vom Volumen abhängigen Energiebetrags [23]. Der vorliegende Deutungsversuch unterscheidet sich von diesen früheren durch seine zwanglose Anwendung auf eine größere Zahl von Strukturklassen. Beispielsweise ergibt sich die Struktur des Hg ziemlich zwanglos aus der Tatsache, daß das Hg-Atom mehr als zwei Elektronen je Atom beisteuert, was aus seinem Verhalten in verschiedenen Legierungen erschlossen werden kann. Außerdem ergibt die Ortskorrelationsdeutung von vornherein eine bestimmtere Erwartung für Achsverhältnis und Stapelfolge. Andere Einflüsse, wie z. B. die BRILLOUIN-Zonenauswirkungen, sollen durch das vorliegende Argument natürlich nicht verdrängt, sondern lediglich ergänzt werden.

Die vorliegende Überlegung hat ferner den Vorteil, daß sie nicht viele spezielle Voraussetzungen benötigt. Man kann sie daher auf andere Strukturgruppen übertragen, für die man einen Ortskorrelationsvorschlag besitzt, und damit den Vorschlag prüfen.

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Magnetic Susceptibility of Alkali Elements

Part I: Sodium and Potassium

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A vacuum CURIE balance was specially designed for the study of magnetic susceptibilities at higher temperatures. With this apparatus the magnetic study of sodium and potassium was made at different temperatures ranging from 32° to 250 °C. Special attention has been paid to the preparation of the specimen. Corrections for all possible errors have been made. The results point out that the susceptibilities of the metals increase with temperature both below and above their melting points. The temperature coefficients of the susceptibility of valence electrons of the two metals are in general agreement with STONER's theory.

The study of the magnetic susceptibility of the alkali metals has assumed great interest in recent years because of the theoretical importance attached to such measurements from the point of view of the weak spin paramagnetism of the conduction electrons in the metals.

The gram atomic susceptibility of a metal is given by $\chi_A = (\chi_A)_i + (\chi_A)_e$ where $(\chi_A)_i$ and $(\chi_A)_e$ are the susceptibilities of the quasi-independent metallic ion and of the free electrons. For systems with spherically symmetrical charge distributions LANGEVIN [1] obtained an expression

$$\chi_A = -\frac{e^2 L}{6 m c^2} \sum_N \overline{r^2}$$

where $\sum_N \overline{r^2}$ is the sum of the mean square radii for each of the extra nuclear electrons. With the introduction of quantum mechanics different methods of calculating $\sum_N \overline{r^2}$ have been suggested. PAULING [2] was the first to compute this value. HARTREE [3] and STONER [4] made use of the distribution of electron density in a spherically symmetrical atom or ion. SLATER [5] gave rules for the calculation of $\overline{r^2}$ for each electron.

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BRINDLEY [6] calculated the susceptibility of various ions making use of the SLATER's method. ANGUS [7] modified SLATER's computations by treating the s and p electrons as separate groups.

PAULI and FRENKEL [8] applied FERMI–DIRAC statistics to the electron gas in a metal in a completely degenerate state for the evaluation of $(\chi_A)_e$. PAULI [8] has deduced the formula $k_0 = 2.209 \cdot 10^{-4}\, n^{1/3}$ for the volume susceptibility of the alkali elements near absolute zero, n being the number of metal atoms per unit volume. He has shown that the alkali metals should all be paramagnetic and that variation of susceptibility with temperature in those elements should be negligible. BLOCH [9] and LANDAU [10] have obtained expressions for the gram atomic susceptibility for free electrons. More recently SAMPSON and SEITZ [11] computed the magnetic susceptibility of lithium and sodium. Their treatment was later modified by MARCH and DONOVAN [12].

A number of recent developments has renewed the interest in the susceptibility of sodium metal, particularly concerning the determination of the three component susceptibilities, namely, the diamagnetism of core electrons, the paramagnetism due to the spin of the conduction electrons and the diamagnetism due to the orbital motion of the conduction electrons. An experimental technique [13] has been developed for measuring the spin contribution directly. PINES [14], TOWNES, HERRING and KNIGHT [15] and KOHN and KJELDAAS [16] have evaluated the spin contribution. With the value of the ion core susceptibility and these recent values for the spin contribution an estimation of the orbital contribution can be obtained if the total static susceptibility is reliably known. SUCKSMITH [17] and RAO and SAVITRI [18] have recorded an increase in the magnetic susceptibility of the alkali metals with temperature both in the solid and liquid states. But others [19] did not observe any change in susceptibility from liquid air temperature up to near the melting point of the metals. A scrutiny of Table 1 shows that the χ values obtained by various authors differ considerably from one another. Hence a careful reinvestigation of the magnetic susceptibility of alkali metals was considered necessary and has been taken up in this investigation.

1. Experimental

a) Preparation of the metal

For magnetic investigation a small quantity of the pure metal has to be taken in a small bulb. For this a pyrex tube of about 8 mm diameter was blown to the shape ABCD (Fig. 1). This was first cleaned and dried and then filled with petroleum ether and kept immersed in a troug containing petroleum. A small piece of

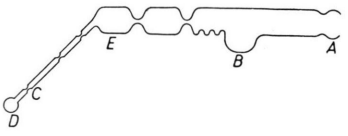

Fig. 1. Apparatus to collect pure metal in the bulb.

A.R. sodium was cut by a sharp knife from the inner core of the sodium bar in the medium of petroleum and introduced into the bulb B. The tube was drained and quickly connected to a high vacuum pumpset by a short rubber tube and the tube was evacuated. When the pressure is of the order of 10^{-4} mm of mercury the tube was gently heated and then the sodium was melted by carefully heating the bulb B. After allowing some time for the removal of occluded gases the tube was isolated from the pump by a stop cock. A gentle horizontal jerk enabled the molten sodium to flow through the constrictions free of any oxide coat. By careful manipulation the small bulb B, about 3 mm diameter, was filled with sodium in a pure state with silvery metallic lustre. The bulb was then sealed off at the point C and the sealed end was drawn in the form of a hook.

The same process could be adopted for potassium. But as its boiling point is low at low pressure the metal was distilled. Under high vacuum, the portion AB of the tube was kept warm and the metal B was heated carefully by a thin flame. The metal vapour condensed on to the cold sides of the tube at E as a mirror coat. When sufficient amount was thus condensed the portion

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E was warmed to melt the metal coat and this was pushed into the bulb D.

b) Determination of magnetic susceptibility

The magnetic susceptibilities were determined by the CURIE retorsion method using a large PYE electromagnet for different field strengths. Thrice distilled A.R. benzene was used as the standard substance whose susceptibility was taken to be $-0.702 \cdot 10^{-6}$. The specific susceptibility is given by the usual expression

$$\frac{d_s}{d_B} = \frac{m_s \chi_s - \varkappa_a v_i}{m_B \chi_B - \varkappa_a v_i'}.$$

This involves a correction for the displaced air. When the study is extended to higher temperatures convection currents set up and will considerably affect the deflections. In order to avoid such disturbances due to convection a vacuum CURIE balance was used. A schematic arrangement of the apparatus is shown in Fig. 2. All the tubes, except the

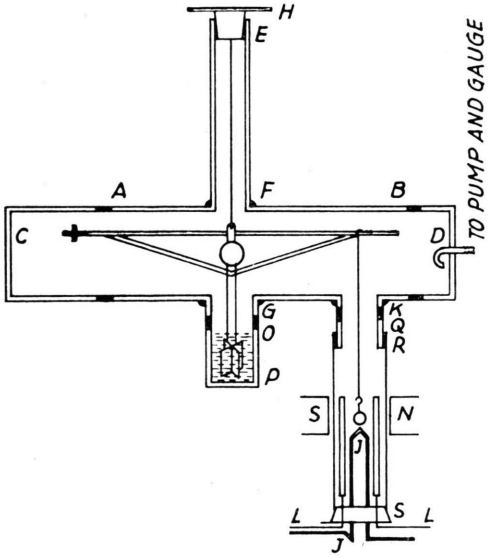

Fig. 2. Vacuum CURIE balance.

glass tube RS, are made of brass. The pole faces were covered by double walled copper metal caps through which cold water was kept circulating when temperature work was in progress. This arrangement was almost completely free from convection currents and was found to give steady and reproducible readings of the spot of light. It is an additional advantage of this arrangement, that the correction for the susceptibility of air becomes zero and the calculations become simpler. The temperature was measured by a thermocouple which was previously calibrated by a preliminary experiment.

c) Correction for ferromagnetic impurities

For each specimen bulb the specific susceptibilities are found at different field strengths corresponding to field currents 3, 4, 5, 6, and 7 amps. According to HONDA [20] $\chi_i = \chi_p + (\sigma m)/H$, where χ_i and χ_p refer to impure and pure substance. At infinite field strength $\chi_i = \chi_p$. Thus by plotting the values of χ_i against $1/H$ the value of χ_p was found by extrapolation.

2. Results

The field strength for the different field currents used varied from 2.64 to 4.20 K.Gauss. The susceptibility values for eleven sodium bulbs and for nine

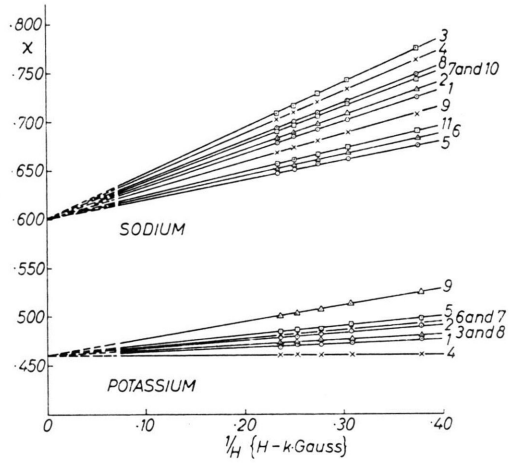

Fig. 3. Plot of χ against $1/H$ for Na and K.

potassium bulbs were determined at room temperature for five field currents. Fig. 3 shows the plot of χ against $1/H$ for all the bulbs. The extrapolated value for pure sodium is 0.600 and that for pure potassium is 0.460.

In Table 1 are given the values of χ_s for the two alkali elements so far obtained by different authors.

[20] K. HONDA, Ann. Phys., Lpz. **32**, 1027 [1910].

Author	χ_s	
	Sodium	Potassium
Experimental		
HONDA[20]	0.51	0.40
OWEN[21]	0.50	0.63
		0.58
BERNINI[26a]	0.54	0.63
SUCKSMITH[17]	0.59	0.51
MCLENNAN, RUEDY and COHEN[19]	0.59	0.45
LANE[22, 23]	0.65	0.64
RAO and ARAVAMUDACHARI[24]	0.60	0.52
KLEMM and HAUSCHULZ[25]	0.664	0.532
BOWERS[26]	0.70	...
Present investignation	0.600	0.460
Theoretical		
SAMPSON and SEITZ[11]	0.700	...
BITTER[26b]	0.210	0.15
BOWERS[26]	0.22	...
	0.40	...
PAULI[8] (calculated)	0.68	0.59

Table 1. χ_s values of two elements obtained by different authors.

a) Temperature variation

Four sodium bulbs and two potassium bulbs were studied at different temperatures from 30 to 250 °C. When the temperature is constant, the space inside is fully evacuated when the spot of light is found to be perfectly steady, even at the highest temperatures used. The temperatures were measured using a thermocouple to an accuracy of about 5 °C. For each specimen and at each temperature χ_s was found at different field currents and the corrected values were found by extrapolating the graphs between χ_s and $1/H$. In Tables 2 and 3 are given the corrected values of the specific susceptibilities for sodium and potassium at different temperatures.

Temp. °C	χ_s of Na (extrapolated)				
	Bulb 3	Bulb 5	Bulb 7	Bulb 10	Mean
30	0.600	0.600	0.600	0.600	0.600
65	0.606	0.603	0.604	0.604	0.604
95	0.606	0.605	0.605	0.605	0.605
110	0.601	0.600	0.600	0.600	0.600
150	0.612	0.610	0.612	0.612	0.612
190	0.615	0.615	0.613	0.615	0.615
250	0.620	0.620	0.620	0.620	0.620

Table 2. χ_s of sodium at different temperatures.

Temp. °C	χ_s of K (extrapolated)		
	Bulb 8	Bulb 9	Mean
30	0.460	0.460	0.460
50	0.465	0.468	0.467
60	0.455	0.458	0.457
100	0.458	0.459	0.459
130	0.460	0.461	0.461
160	0.462	0.462	0.462
190	0.463	0.464	0.464
220	0.465	0.465	0.465
250	0.466	0.467	0.467

Table 3. χ_s of potassium at different temperatures.

3. Discussion

The atomic weights of sodium and potassium are 22.99 and 39.09 respectively and their gram atomic susceptibilities work out to be 13.79 and 17.98. The ionic susceptibilities suggested by TREW[27] as the most probable values for Na^+ and K^+ are -6.8 and -14.9. Hence the contribution to the susceptibility of a gram atom of sodium by the valence electron is 20.59 and for potassium the value is 32.88 at room temperature. According to LANDAU[10] the gram atomic susceptibility $(\chi_A)_e$ of the free electrons in a gram atom of the metal is given by the expression $(\chi_A)_e = 32 \cdot 11\,(q/V_0) \cdot 10^{-6}$ where q is the number of free electrons per atom and V_0 the width in volts of the energy band occupied by the electrons in the completely degenerate state. From this expression, the value of V_0 can be calculated. In Table 4 are given the values of V_0 thus calculated.

The last two columns indicate a narrowing of the energy band of the collective electrons as suggested by STONER[28].

The nature of the variation of the susceptibility of these two elements with temperature is in agreement with the observation of SUCKSMITH[17]. In the case of potassium the variation of χ_s with temperature is small compared to the variations obtained in the case of sodium and rubidium[29]. The variation of the susceptibility of the alkali metals has been

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Element	χ_A	$(\chi_A)_{ion}$	$(\chi_A)_e$	V_0	Calculated energy bandwidth in volts[21]
Sodium	13.79	− 6.8	20.59	1.56	3.15
Potassium	17.98	− 14.9	32.88	0.98	2.04

Table 4. $(\chi_A)_e$ and V_0 for the two elements.

Element	Temp. range °C	$(\chi_A)_e$	$\Delta(\chi_A)_e$	$\frac{\Delta(\chi_A)_e}{(\chi_A)_e \Delta T}$	$\frac{2}{3}\alpha_v$
Na	110—250	20.59	0.47	1.60×10^{-4}	1.80×10^{-4}
K	100—250	32,85	0.31	0.62×10^{-4}	1.90×10^{-4}

Table 5. Temperature coefficient of $(\chi_A)_e$.

theoretically discussed by STONER [30] on the basis that for these metals the conditions approach closely those for which the free electron calculations should apply. He has shown that the temperature coefficient of the paramagnetic contribution of the free electron is nearly equal to two thirds the coefficient of cubical expansion.

$$\frac{\Delta(\chi_A)_e}{(\chi_A)_e \Delta T} = \frac{2}{3}\alpha_v .$$

From the values recorded in the previous tables the temperature coefficient of $(\chi_A)_e$ for the two metals in the liquid state are calculated and given in Table 5.

The values in the last column are taken from STONER [30]. It could be seen that the values in the last two columns are in good agreement in so far as the order of the value is concerned, thus lending support to STONER's theory.

[30] E. C. STONER, Proc. Roy. Soc., Lond. A **152**, 672 [1935].

Magnetic Susceptibility of Alkali Elements

Part II: Liquid Alloys of Sodium and Potassium

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(Z. Naturforschg. **13 a**, 455—458 [1958]; eingegangen am 7. November 1957)

Alloys of sodium and potassium were prepared in vacuum in a specially blown pyrex glass apparatus. Several bulbs containing these alloys of different compositions have been studied at temperatures ranging from 30 ° to 250 °C. The compositions of these alloys have been determined by gravimetric method. The results show that for the alloys of all compositions the additivity law is obeyed both at room temperature and at higher temperatures. No evidence for the formation of the compound Na_2K could be detected from the magnetic study.

Sodium and potassium are known to form a series of alloys which are mostly liquid at ordinary temperatures. The studies on the heats of formation [1–5], melting point determinations [6–9] and viscosity measurements [10–11] of these alloys have all pointed to the conclusion that a compound represented by the formula Na_2K is formed. KURNAKOFF and PUSHIN [6] have further suggested that the composition corresponding to the formula NaK represents an eutectic.

X-ray studies of these alloys were made by some

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