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.

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Magnetic Susceptibility of Alkali Elements

Part II: Liquid Alloys of Sodium and Potassium

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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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authors[12–14]. BANERJEE[12] explained the patterns he obtained on the assumption of the formation of the compound Na_2K. He further concluded that all alloys of different compositions contained this compound and that the excess of sodium or potassium remained dissolved in the above compound. The results obtained by HEAPS[13] led to conclusions which did not contradict BANERJEE's inferences. BOHM and KLEMM[2] found evidence for such a compound formation at −70 °C. Quite recently GINGRICH and HENDERSON[14] made a detailed study of the diffraction of X-rays by liquid alloys of Na-K of seven different compositions at 115 °C. They could not find conclusive evidence for the existence of the compound Na_2K though they did not rule out the possibility of the presence of weakly associated groups of atoms.

Very little work has been done on the magnetic properties of these alloys. BOHM and KLEMM[2] have studied the Na-K system at temperatures 20 °, −78 °, and −183 °C and their results show that at −78 ° and 20 ° the system Na-K behaves additively in its magnetic properties. At −183 °C the alloys were found to be less paramagnetic. This lowering in the χ value, though very small, was attributed to the possible formation of the compound Na_2K.

Thus the studies on the different aspects of the Na-K alloys seem to give to some extent contradictory conclusions with regard to the existence of the compound Na_2K. Hence the present investigation is taken up with a view to make a detailed magnetic study of Na-K systems of different compositions at temperatures ranging from 30 ° to 250 °C.

1. Experimental

a) Preparation of the alloy

Sodium and potassium used in this investigation were of the highest purity. The alloys were prepared in vacuum with a specially prepared pyrex apparatus (Fig. 1). Small pieces of the metals, cut from the inner core of the metal blocks, were introduced into the bulb B_1 of the tube which was then quickly evacuated warming the tube to ensure perfect dryness. Isolating the tube from the pump, the metals were just melted and the bulb was shaken to make the molten metals mix well. This was jerked into the bulb B_2 through the constrictions which collected any oxide coat and the tube sealed off at A. The bulb B_2 was shaken well to ensure uniform composition of the alloy, which was then transferred to B_3. The tube was sealed off at B and the alloy in B_3 was given a further shaking and a small portion of it was jerked into the bulb B_4. With a pointed flame the bulb B_4 was sealed at D and the sealed end was drawn into a hook. Also the bulb B_3 was sealed at C. The alloy in B_4 was used for magnetic investigation and that in the bulb B_3 was used for chemical analysis. In this way several bulbs containing alloys of different compositions were prepared and used.

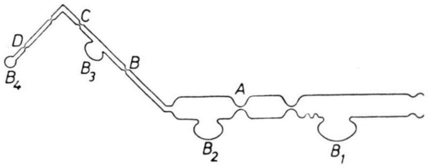

Fig. 1. Apparatus to collect alloys in the bulbs.

b) Analysis of the alloys

The composition of each alloy was found gravimetrically. The method adopted was to dissolve the alloy in water and to precipitate $K_2Na[CO(NO_2)_6]$, H_2O using sodium cobaltinitrite as reagent. From the weight of the precipitate obtained the weight of the potassium content in the alloy was calculated. *A duplicate was conducted in every case.* In no case the weights of the precipitates differed by more than 1% and in many cases the difference was less than 0,3%.

c) Determination of magnetic susceptibility

The specific paramagnetic susceptibilities of the alloys were found by the CURIE retorsion method using the vacuum arangement described in part I. For every alloy χ values were determined for five different field currents and a correction for any ferromagnetic impurities was applied graphically.

d) Temperature study

Seven bulbs containing alloys of different compositions were studied at different temperatures up to 250 °C and at each temperature the values of χ were found for five field currents and the values for the pure alloys were obtained by extrapolating the graph between χ and $1/H$.

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Bulb No.	Wt.% of sodium		χ of alloys at							
			30° C	60	90	120	150	180	210	250
1	81.44	Extrapolated	0.570	0,572	0,575	0,575	0.577	0.580	0.585	0.590
		Additive	0.574	0.576	0.577	0.575	0.580	0.584	0.588	0.592
2	74.55	Extrapolated	0.560	0.562	0.570	0.570	0.572	0.575	0.575	0.575
		Additive	0.564	0.566	0.567	0.565	0.570	0.574	0.578	0.581
3	55.20	Extrapolated	0.538	0.540	0.540	0.542	...	0.545	0.547	...
		Additive	0.537	0.539	0.539	0.537	...	0.545	0.548	...
4	49.35	Extrapolated	0.526	0.527	0.530	0.530	0.531	0.535	0.538	0.540
		Additive	0.529	0.531	0.530	0.529	0.533	0.537	0.540	0.542
5	33.77	Extrapolated	0.505	0.505	0.505	0.506	0.508	0.510	0.510	0.513
		Additive	0.507	0.509	0.507	0.507	0.510	0.513	0.516	0.519
6	24.65	Extrapolated	0.495	0.496	0.498	0.500	0.498	0.500	0.501	0.505
		Additive	0.495	0.496	0.494	0.494	0.497	0.499	0.502	0.505
7	22.03	Extrapolated	0.491	0.491	0.492	0.492	0.495	0.496	0.492	...
		Additive	0.491	0.492	0.490	0.490	0.493	0.496	0.498	...

Table 1. Susceptibility of alloys at different temperatures.

2. Results

The alloys obtained in most of the bulbs were either in a semisolid or liquid state. That they were free from any trace of oxide is shown by their metallic lustre and bright meniscus.

In Table 1 are recorded the results obtained at different temperatures for the alloys in the seven bulbs. The additive values for each alloy and for every temperature were calculated making use of the respective values of Na and K reported in Part I.

3. Discussion

When two metals are mixed it may result in the formation of a primary or secondary solid solution or an intermetallic compound. In the case of the primary solid solutions the structure remains unchanged. In secondary solid solutions the structure differs from those of parent metals. But there is no indication in these cases of any electron exchange to form a molecule. When the two metals form an intermetallic compound, electron exchange or sharing takes place and a compound molecule is formed between the atoms of the two metals. The properties of these compounds are entirely different from those of the pure metals. Norbury[15] has shown that graphs between concentrations and temperature coefficient of resistance exhibit sharp maxima at concentrations at which solid solutions or intermetallic compounds are developed. X-ray diffraction patterns are undisturbed in the case of primary interstitial solid solutions. With secondary solid solutions the two diffraction patterns characteristic of the metals are superposed. But in the case of intermetallic compounds entirely different patterns are recorded. Thus electrical conductivity and X-ray data offer convincing evidences regarding the various types of the alloys.

The data available concerning the heats of formation, melting point determinations and viscosities of Na-K alloys lead largely to the conclusion that a compound Na_2K is formed. It was further suggested[6] that the alloy of composition NaK represents an eutectic.

The X-ray studies of these alloys give only an inconclusive evidence for the compound formation. Except the results of Banerjee[12], those of others do not give definite evidence for the formation of such a compound. Bohm and Klemm[2] assert that the compound is formed at -70 °C though the patterns obtained at room temperature were not quite sharp. But Gingrich and Henderson[14] have pointed out that the observations on which Banerjee[12] based his conclusions for the existence of the compound Na_2K in the liquid state were not convincing. These authors have studied the alloys at 115 °C at which temperature they could point out a possibility of weak atomic associations only.

Results given in Table 1 point out clearly that the values of the magnetic susceptibilities of the Na-K alloys vary linearly with concentration. This can be taken as a definite indication to show that no compound is formed between these two metals. It may also be taken to indicate a remote possibility of even the formation of secondary solid solution. Of course this does not preclude the possibility of weak atomic

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associations suggested by GINGRICH and HENDERSON[14].

The study of the magnetic susceptibilities of these alloys at different temperatures show that even if there were weak atomic associations at lower temperatures, such associations do not affect the additive properties of the alloys, as these weak associations would certainly break at higher temperatures. BOHM and KLEMM[2] have also studied the magnetic properties of the alkali metals and their alloys at some definite temperatures. They have shown that at $-78\ ^\circ$C and $20\ ^\circ$C the alloys obey additivity, though at $-183\ ^\circ$C they have recorded a small fall in the paramagnetism of the alloy of composition Na_2K. But this lowering in the value was within their experimental error. With Na_2Cs system this lowering was appreciable at $100\ ^\circ$C. If this lowering in the paramagnetism of the alloy is an indication for the formation of a compound there is no such definite indication for Na-K system. In this respect their results are in agreement with those of the present investigation. Hence the magnetic study of the Na-K system seems to favour the idea that these alloys in the liquid state behave more or less like liquid mixtures, with no great structural change or compound formation.

Ultrarotes Spektrum und Trägerbeweglichkeit im Eigenleitungsbereich von Silicium

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An eigenleitendem Silicium wurden im Temperaturbereich zwischen 300 und 1000 °K Leitfähigkeit und Ultrarotabsorption gemessen, letztere zwischen 1,0 und 3,5 μ. Die Wellenlängenabhängigkeit entspricht der DRUDE–ZENER–FRÖHLICHschen Theorie für die Absorption freier Ladungsträger. Dieser Theorie entsprechend wird durch die Quotientenbildung beider Meßwerte die zunächst unbekannte Trägerzahl eliminiert und quantitativ die Elektronenbeweglichkeit und ihre Temperaturabhängigkeit gewonnen ($b_E\,[\mathrm{cm^2/V\,sec}] = 1{,}85 \cdot 10^6\, T^{-1{,}5}$). Auch die sich daraus ergebende Trägerzahl ($N_E\,[\mathrm{cm^{-3}}] = 5{,}71 \cdot 10^{16}\, T^{1{,}5} \exp[-1{,}16/2\, k\, T]$) stimmt mit der von anderen Autoren aus dem HALL-Effekt bestimmten überein. Die Theorie wird damit der experimentellen Absorption im Durchlaßbereich jenseits der Bandkante gerecht. Aus der Verschiebung der Bandkante mit der Temperatur wird die Temperaturabhängigkeit des Bandabstandes ermittelt.

Die durch die Anwesenheit freier Ladungsträger bedingte optische Absorption von Germanium im ultraroten Spektralbereich jenseits der Bandkante übersteigt die aus elektrischer Leitfähigkeit und Trägerzahl mit der DRUDE–ZENER–FRÖHLICHschen Theorie errechneten Werte um mehrere Größenordnungen[1]. Die effektiven Massen der Träger gehen in den Absorptionskoeffizienten quadratisch ein, so daß bei n-Germanium eine brauchbare Erklärung[2] durch Verringerung der effektiven Elektronenmasse auf $0{,}1\ m_0$ möglich ist. In der Eigenleitung ist jedoch die Abweichung noch 20-mal größer. Hier hat erst die Berücksichtigung der Entartung des Valenzbandes und die daraus folgende Anwesenheit von zwei verschiedenen Löchermassen und Dichten eine befriedigende Übereinstimmung herbeigeführt[3].

Bei Silicium waren analoge, aber viel kleinere Abweichungen im Fremdleitungsbereich bekannt[1]. Da in der Eigenleitung der Einfluß der Träger am reinsten und reproduzierbarsten beobachtet werden kann, anderseits Zyklotronresonanzmessungen bei tiefen Temperaturen auch hier die Entartung des Valenzbandes gezeigt hatten[4], lag es nahe, den Ansatz mit drei Ladungsträgerarten auch hier zu prüfen.

Bei der kleinen Abweichung von Experiment und Rechnung verliert die Prüfung jedoch erheblich an Überzeugungskraft infolge der Unsicherheit in der

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