This provides a relatively simple grouping of ions which includes the nearest and next nearest cation neighbors. Each anion is surrounded by three cations which lie nearly in a plane and of which two are equidistant and the other at a 20% greater distance from the anion. From the previous discussion it is apparent that the singly occupied d_{z^2} orbital is associated with the longer cation-anion separation while the unoccupied $d_{x^2-y^2}$ orbital is associated with the shorter ones. It is observed that the two cations with short cation-anion separations are coupled antiferromagnetically in both structures. In CrF_2 these cations are next nearest neighbors (corner and body center sites) while for $CrCl_2$ they are nearest neighbors (corner sites along c). In the former the Cr-F-Cr angle is large enough (132°) for indirect exchange involving σ-type overlap of the orbitals but in the latter the relevant angle is so small (92°) that some other mechanism is probably required. One is forced then to consider such mechanisms as indirect exchange of the $t_{2g}-p_\pi$ type or direct exchange involving t_{2g} cation orbitals. An interpretation of these magnetic structures based on a comparison of the relative strengths of such interactions is at the present somewhat speculative and must await further developments of both theoretical and experimental nature.

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Atomic Heat of Sodium Metal from 0.4 to 2°K*

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The atomic heat of sodium metal was measured from 0.4 to 2°K using the magnetic refrigerator calorimeter. The experimental data is given by $C=1.32T+0.485\ T^3$ millijoule/mole-°K. No anomaly is observed in this temperature range. The experimental value of the electronic specific heat and the Pauli spin paramagnetism measured by Schumacher and Slichter are used for comparison with the electronic band theory of sodium and with those modifications introduced by electron-electron and lattice-electron interactions.

INTRODUCTION

THE alkali metals, having one valence electron per atom and simple crystal structures, are expected to agree rather well with the various theoretical models for their solid-state properties. The suggestion by Rayne[1] that an anomaly occurs in the specific heat of sodium metal near 0.7°K does not have an explanation in terms of these models. Since the magnetic refrigerator calorimeter[2] is well adapted for specific heat measurements on large samples in the temperature region below 1°K, an investigation of the specific heat of sodium metal under more favorable experimental conditions than used previously was undertaken below 1°K.

EXPERIMENTAL

In order to minimize spurious contributions to the apparent heat capacity of the sodium sample, considerable care was taken in the preparation of the sample. A.C.S. reagent grade sodium metal of stated purity 99.99% was vacuum distilled in order to remove gaseous impurities and inclusions of the oxide. Since sodium metal readily attacks glass, the distillation was carried out in a stainless steel assembly which permitted the sodium to be deposited directly into a thin-walled copper vessel. After deposition of the liquid metal into the container, the temperature was gradually reduced to allow the sample to anneal. Further handling of the sample was done in an argon atmosphere. A large sodium metal sample of 2.71 moles was prepared in a 2.11-mole copper vessel in this manner.

Temperature measurements were made with a Speer 470 ohm-1/2 watt carbon resistor and heat was supplied electrically by a Manganin heater. The carbon resistor and heater coil were inserted in separate copper inserts which were a part of the copper vessel as shown by K and L in Fig. 1. Thermal bonding to the copper was provided by General Cement No. 56-2 varnish. Since the heat capacity of this assembly of heater, thermometer, and copper container was estimated as 20% of that of the sodium, a heat capacity measurement was made prior to filling. The sample assembly is rigidly mounted inside a copper shield as shown in Fig. 1, and the shield is cooled to 0.3°K by means of the magnetic refrigerator.[2] Over the temperature range in which heat capacity measurements were made the effects of the residual

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[*] This research was supported in part by the U. S. Air Force under a contract monitored by the Air Force Office of Scientific Research of the Air Research and Development Command.

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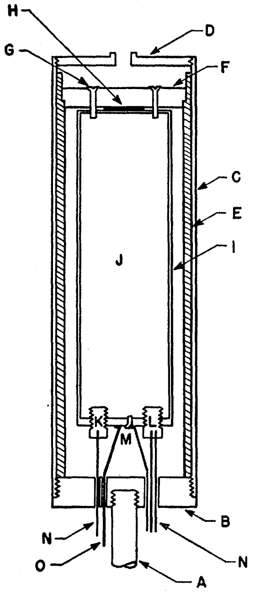

Fig. 1. Sodium sample assembly. *J*—sodium sample; *I*—copper sample container; *E*—fiber mount; *C*—copper sample shield; *K*—thermometer; *L*—heater; *O*—thermal link.

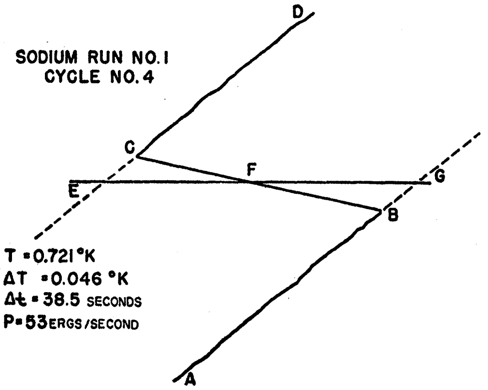

Fig. 2. Heating cycle. *ABCD*—temperature record during a heating cycle; *BC*—heat input of 53 ergs/second; *F*—mean temperature of 0.721°K; *EFG*—temperature change $\Delta T=0.046°\text{K}$.

helium gas is minimized by the low temperature of the shield. Thermal contact is made between the shield and sample container via No. 20 copper wire with a ratio of area to length of $A/L \simeq 5\times 10^{-4}$ cm. Thermal contact between the sodium metal and either the heater or thermometer was assured by the direct deposition of the liquid metal on their copper jackets. The difference in the thermal expansion coefficient of copper and sodium insured that this thermal contact would be maintained to the lowest temperatures.

Heat capacity measurements were made from the change in the rate of cooling by the introduction of known amounts of Joule heating.[3] A continuous record of the resistance thermometer emf was obtained with a recording Brown potentiometer (0–100 microvolts) in series with a Rubicon Type *B* potentiometer. A heating cycle at 0.72°K is shown in Fig. 2. From *A*-*B* the sample cooled at the rate of 0.22×10^{-3} degree/second. The heater was switched on at *B* and off at *C* providing 2040 ergs of heat in a period of 38.5 seconds. *C*-*D* represents the subsequent cooling rate. *EFG* gives the net change in voltage across the carbon resistance thermometer, and *F* was taken as the average voltage. This change corresponds to a change in temperature $\Delta T=0.046°\text{K}$ at a mean temperature of 0.72°K.

Carbon resistance thermometers were calibrated against the vapor pressure of the helium bath in the 1–4°K temperature range using the T_{L55} scale.[4] The calibration data was fit to the equation

$$T=(a\log_{10}R)/(\log_{10}R\text{-}b)^2, \qquad (1)$$

with $a=0.11209$ and $b=2.69277$ for the sodium run. A shift of the order of 1% in *a* and *b* occurred between the run on the empty and filled container. For temperature measurements below 1°K the temperature was obtained by an extrapolation of Eq. (1) down to 0.35°K. At this temperature the sample shield thermometer agreed with the magnetic susceptibility measurements on the manganous ammonium sulphate reservoir salt to within 10 millidegrees. The sample thermometer reached a lowest temperature within 20 millidegrees of that indicated by the magnetic thermometer and the extrapolated temperatures of the sample and sample shield thermometer agreed within 10 millidegrees at this low temperature. The error made in estimating the thermodynamic temperature from the magnetic susceptibility measurements is of this same order of magnitude, i.e., the shape correction[5] and the $(T_{\text{Lor}}^{*}-T)$ correction.[6] Thus errors in temperature measurement of the order of 5% at 0.4° and 2% at 0.65° are expected.

Results of a least squares analysis of 40 data points for the copper container plus sodium sample gave a total heat capacity of

$$C_{\text{total}}=5.39T+1.500T^3$$

millijoule/°K. A separate analysis on the heat capacity of the copper container below 1°K yielded a term linear in temperature with $\gamma_{\text{Cu}}=0.80$ millijoule/mole−°K. This value is intermediate to the experimental values given by Rayne[1] and Estermann, Friedberg, and Goldman.[7] The value of $\theta_D=348°\text{K}$ was taken from the latter reference. Subtraction of the heat capacity of the copper vessel assembly yields the following equation for the atomic heat of sodium metal,[8]

$$C_{\text{Na}}=1.32T+0.485T^3(\text{millijoule/mole°K}). \qquad (2)$$

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[8] This value for the atomic heat of sodium metal was reported by us at the Fourteenth Calorimetry Conference (unpublished). N. E. Phillips reported at this conference a value of $\gamma=1.45$ and $\theta_D=152°\text{K}$. In a recent private communication W. H. Lien and N. E. Phillips report $\gamma=1.45$ and $\theta_D=156°\text{K}$.

The lattice or cubic term in the atomic heat yields a $\theta_D = 158$ which is in excellent agreement with the value obtained by Roberts[9] at higher temperatures. The atomic heat for sodium metal is shown in Fig. 3 and the experimental points indicate the accuracy.

DISCUSSION

Measurements of the atomic heat of sodium below 2°K allow the coefficient of the linear term, γ, to be determined with considerable accuracy. From Eq. (2) a value of $\gamma = 1.32$ millijoule/mole−°K is obtained. Assuming one valence electron per atom, this can be compared with the Sommerfeld free electron model of $\gamma_f = 1.095$, where the density at 77°K is used ($\rho = 1.0066$ g/cm^3).[10] If the lattice structure is introduced via a density of states or effective mass approximation the two values are in agreement with $m^*/m = 1.21$. Either the free electron model or the effective mass model lead to a ratio of the Pauli spin paramagnetism to the specific heat per unit volume given by,

$$(\chi_0/\gamma_0) = (3\mu_B{}^2/\pi^2 k^2).$$

The measurements of Schumacher and Schlicter[11] of the spin paramagnetism of $\chi_p = 0.95 \times 10^{-6}$ cgs by electron resonance when combined with the above value of γ allow the experimental ratio to be computed, and a value of

$$(\chi/\chi_0)/(\gamma/\gamma_0) = 1.20$$

is obtained. The deviation of this ratio from unity is a measure of the failure of the free electron model and those electronic band models in which the predominant effect is a change in density of states at the Fermi surface or an effective mass modification. Buckingham and Schafroth[12] have estimated the effect of the lattice-electron interaction on the atomic heat and spin paramagnetism. Both are increased over the free electron values by $(1+f)$, $f \sim 0.2$. This correction improves the agreement with the experimental data, but fails in the same manner as the effective mass modification to account for the ratio between spin paramagnetism and atomic heat. An improvement in agreement between the experimental ratio and the theoretical model requires the introduction of the electron-electron interaction.[13] The calculation of Pines[14] in which the effect of electron-electron interaction is taken into account by means of the "collective electron" approach is in poor agreement. The change in the density of states reduces the specific heat below the free electron value while the short range Coulomb correlations between electrons of antiparallel spin and the correlation energy of a free electron gas combine to increase the spin paramagnetism. The agreement with the experimental data can be considerably improved by combining the results of Buckingham and Schafroth with those of Pines. An increase in the value of β by 10% in the "collective-electron" approach and then direct multiplication by $(1+f)$ for the lattice-electron interaction yields good agreement for both γ and χ with an effective mass ratio of $m^*/m = 0.98$ taken from cohesive energy studies. Since the validity of this procedure may be questionable, it is not pursued in this paper.

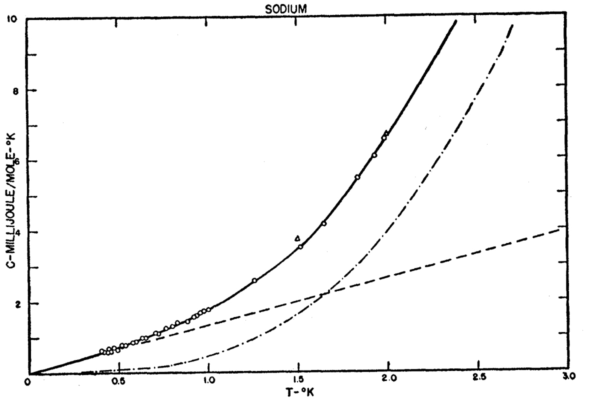

FIG. 3. Atomic heat of sodium. ○—experimental data; △—data of Roberts, reference 9.

Below 36°K a change in crystal structure from body-centered cubic to hexagonal close packed[15] is expected to occur for a part of the sodium sample. Since no change in density occurs during the transformation, the effect on the electronic specific heat is small; and since the estimated fraction of hcp lattice is of the order of 5% no detectable effect is expected. Martin[16] estimates the energy involved in the transition as 400 joules/mole. Sample isolation below 1°K indicates that no anomalous heating occurs, and that the rate of transformation is negligible below 1°K. The lattice specific heat is also insensitive to the transfer of a small percentage of the material to the hcp structure.

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