PHYSICAL REVIEW B VOLUME 1, NUMBER 6 15 MARCH 1970

Electronic Specific Heat of Vanadium Chromium Hydride*

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(Received 12 August 1969)

Electronic specific-heat coefficients γ have been measured for five samples of the $V_{1-x}Cr_xH_y$ system. Results on two samples with $y=0$ agree with known values of γ for $V_{1-x}Cr_x$ alloys. All hydride samples $y\neq 0$ have a decrease in γ compared to nonhydride samples. The plotted points for hydride and nonhydride samples fall very close to a single curve of γ versus $\mathfrak{z}$, the electron per atom ratio, when $\mathfrak{z}$ is determined by $\mathfrak{z}=5(1-x)+6x+y$. Results indicate that the rigid-band model is useful in qualitative interpretation of the effects of hydriding transition metals. The fact that γ depends upon $\mathfrak{z}$ and not upon relative amounts of Cr or H supports the concept that the hydrogen atom contributes its electron to the host-metal conduction band.

I. INTRODUCTION

MANY transition metals are known to absorb hydrogen exothermically into interstitial sites. While lattice constants, activation energies, neutron spectra, and other measurements are available for these metal hydrides, the nature of the metal-hydrogen bond has been in question. (Other elemental hydrides are more easily classified. For example, the alkali-metal hydrides are generally considered to be ionic with negative hydrogen ions.) Recently, a number of these transition-metal hydrides have been investigated using nuclear-magnetic-resonance (NMR) techniques.[1–4] NMR and other studies[5] of these hydrides suggest that the hydrogen contributes its electron to the conduction band of the host transition metal and exists as an interstitial positive ion. With this assumption and a rigid-band model, it can be seen that the alloying of hydrogen with a transition metal should affect the conduction band as if another metal with one extra electron per atom were alloyed with the original metal.

This study was undertaken in order to further investigate the transition-metal hydrides in the hope of developing a better understanding of the role of the hydrogenic electron. In this study, the changes in the electron specific heat on alloying chromium with vanadium are compared to the changes on adding hydrogen to the vanadium lattice. Comparisons are made on the basis of information gained from samples prepared in the ternary alloy system: vanadium-chromium-hydrogen. These samples are designated $(V_{1-x}Cr_x)H_y$.

There are several reasons for selecting the V-C alloy system. Chromium is adjacent to vanadium in the periodic table having one extra conduction electron per ion. When alloyed, the two metals form a bcc solid solution over the entire concentration range. Experiments by Butterworth[6] indicate that one can assume a rigid-band model over most of the concentration range. Thus, the addition of chromium or hydrogen to vanadium should not greatly affect the band structure but only change the number of conduction electrons per atom, $\mathfrak{z}$. The electrons–per–transition-metal atom ratio for the V-Cr-H alloys is computed as

$$\mathfrak{z}=5(1-x)+6x+y=5+x+y\,.$$

In the range $5.0\leq\mathfrak{z}\leq 5.6$, the electron density of states at the Fermi level for the VCr_x alloys has a strong monotonic dependence on the ratio of electrons per atom.

Another reason for choosing this system is that there is a large amount of information available for vanadium, vanadium chromium, and vanadium hydride. This work has been done by Drain,[7] Butterworth,[6] Zamir,[1] Cheng,[8] and others, and includes NMR, electron specific heat, and magnetic susceptibility data. Striking similarities between the NMR properties of vanadium chromium and vanadium hydride led to the selection of this system.

In other experiments,[9] the effects of hydrogen on the metal conduction band was observed by measuring the Knight shifts and spin-lattice relaxation times T_1 for vanadium in the ternary alloys as a function of hydrogen and chromium concentration. These measurements indicate that the NMR properties depend primarily on the effective number of electrons per atom and not on the relative proportions of hydrogen and chromium. In vanadium metal, however, the Knight shift and lattice-relaxation times are not simple functions of the electron density of states at the Fermi surface due to the many mechanisms involved. To determine more

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* Supported in part by the Advanced Research Projects Agency through the Materials Science Center at Cornell, MSC Report No. 1192 and by the National Science Foundation through Grant No. GP-9343. Based in part upon the Ph.D. thesis of one of the authors (D. Rohy), Cornell University, 1968 (unpublished).

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directly the effect of the hydrogen electron on the electron density of states at the Fermi surface, we measured the electronic specific heat of several alloys and alloy hydrides.

II. EXPERIMENTAL

The Dewar, cryostat, and pumping systems were of conventional design. The cryostat is shown in Fig. 1. The cryostat was designed to allow the experimenter to change samples quickly and frequently. Nylon screws with sharpened tips were used to secure the samples in the sample can. Mounting the samples in this way proved superior to nylon thread suspension because it offered adequate thermal isolation with a lack of vibration, a potential source of heating energy. A low-temperature optical baffle in the pumping line inhibited high-energy gas molecules from striking and warming the sample.

Heating power was supplied to the sample via 300 Ω of $2\frac{1}{2}$-mil manganin wire cemented directly to the sample. A timing circuit produced both the heater-current pulse and a pulse of identical duration to a six-figure time-interval unit. Heating power dissipated in the sample was calculated from the heater wire resistance, current, and the length of the heat pulse. The current was determined by measuring the potential drop across a 0.5% precision 50-Ω resistor.

A partial pressure of helium gas was used as a thermal shunt to cool the samples to a 4.2°K. To reduce the possibility of adsorbing significant quantities of helium on the sample, the exchange gas was removed at that temperature and the sample can was pumped continuously thereafter. Then the sample was cooled over a long period of time (6–8 h) to 1.7°K via the thermal conductivity of the lead-in wires.

It was found to be necessary to use the heating coil to supply bursts of energy to the sample during the cooling period to remove any helium gas adsorbed on the surface. The minimum amount of heat needed to drive off the helium was determined empirically. With the procedure developed, experimental results were reproducible and in agreement with available published data[8] for some of the alloys measured.

During the experiment, heat pulses were applied with sufficient energy to raise the sample temperature approximately 100 mdeg per pulse. Temperature was measured with a calibrated germanium resistor attached directly to the sample. Calibration was accomplished by recording the germanium resistance at various temperatures using the 1958 standard helium-vapor pressure table as a reference. An ac resistance bridge operated at 33 cps (Hz) was used to measure the resistance of the germanium thermometer. About 40 heat pulses raised the sample temperature from 1.7 to 4.2°K, producing as many data points.

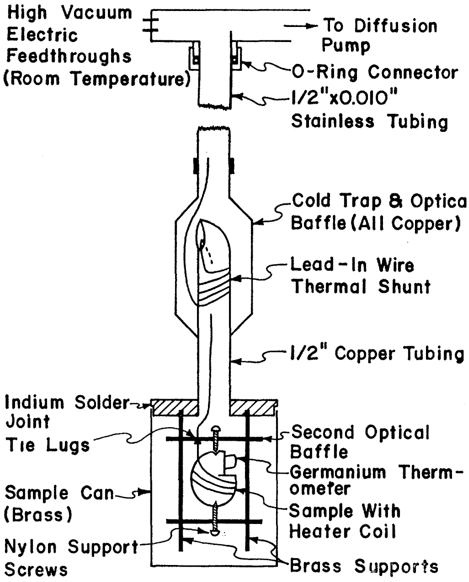

FIG. 1. Diagram of cryostat used in specific-heat measurements.

Due to the thermal conductivity of the lead-in wires, the sample cooled after each heat pulse. While the cooling was not a significant fraction of the temperature increment, it was minimized by allowing the helium bath to warm during the experiment. The bath temperature was always less than that of the sample, however. To correct for the residual temperature drift, the resistance of the germanium was measured five or six times at 10-sec intervals after each heat pulse. These data were extrapolated to obtain the temperature of the sample directly after the heat pulse.

No systematic corrections for heat capacity of the calorimeter were made to the specific-heat data. The specific heat of the lead-in wires, heater wire, and germanium thermometer were considered and found to be small (less than 1.0% of the sample electron specific heat) in comparison with the relatively large electron specific heats of the vanadium alloys. These corrections were included in the over-all experimental error of about 3%.

Two vanadium-chromium alloy samples of about 25 g each were prepared by Material Research Corporation to a tolerance of ±0.002 g. The $V_{0.8}Cr_{0.2}H_{0.1}$ sample was hydrided in a hydrogen furnace at 1000°C with the net hydrogen absorption computed from the change in weight. A destructive test, performed later, indicated a fairly uniform distribution of hydrogen in that sample. The vanadium-hydride sample $VH_{0.5}$ and the alloy hydride sample $V_{0.8}Cr_{0.2}H_{0.3}$ were prepared from vanadium pellets made by Atlantic Equipment Engineers with nominal purity of 99.9%. To form the $VH_{0.5}$ sample, the vanadium pellets were hydrided and crushed to a maximum particle size of 177 μ. The hydrogen was thoroughly removed and the sample then rehydrided to 0.48 hydrogen per vanadium. A cylindrical pellet, $\frac{1}{2}$ in. in diameter, was formed from this powder under the application of high pressure. The pellet was well-formed and held together without the use of a chemical binder. The particles were packed to a density 75% of that of the pure metal. A thin coat of varnish was added to the surface to avoid sample loss due to abrasion. The $V_{0.8}Cr_{0.2}H_{0.3}$ hydride was formed in a manner similar to the $VH_{0.5}$ sample described above.

III. DISCUSSION

In the free-electron model, the electronic specific heat is related to the density of states by

$$C_e=(2\pi^2/3)k_B{}^2N_{\text{fe}}(0)T\,,$$

where $N_{\text{fe}}(0)$ is the free-electron model density of states at the Fermi surface.

The total density of states in the real metal is affected by electron-electron and electron-phonon interactions. These effects have been estimated by McMillan[10] for the $V_{1-x}Cr_x$ alloys. He expresses the electronic specific heat in terms of the band-structure density of states $N_{\text{bs}}(0)$ times an enhancement factor $(1+\lambda)$ due to the electron-phonon interaction. Then,

$$C_e=(2\pi^2/3)\,k_B{}^2N_{\text{bs}}(0)(1+\lambda)T=\gamma T\,.$$

In $V_{1-x}Cr_x$ alloys, the value of λ determined by McMillan varies smoothly from $\lambda=0.60$ for pure vanadium to $\lambda=0.33$ for $V_{0.5}Cr_{0.5}$.

In this alloy system, the measured value of γ changes from 9.9 mJ/mole °K² for pure vanadium to 4.85 mJ/mole °K² for $V_{0.5}Cr_{0.5}$. Over this range, the enhancement factor $(1+\lambda)$ changes from 1.6 to 1.33, while the measured γ changes by almost a factor of 2. Most of the change in γ is due to changes in $N_{\text{bs}}(0)$ across the alloy range. Therefore, γ is a good indicator of changes in the band-structure density of states even before electron-phonon corrections are made. We assume that λ does not change appreciably upon the addition of hydrogen and that in the alloy hydrides γ is still a good indicator of changes in the electron density of states.

If the hydrogen were to exist in the metal as a negative ion, then it would have the effect of depleting the number of electrons in the conduction band. For any $V_{1-x}Cr_x$ starting sample, addition of hydrogen would then cause a decrease in $\mathfrak{z}$ and an increase in γ. On the other hand, if, as assumed, hydrogen exists as a positive ion, it would yield an increase in $\mathfrak{z}$ and a decrease in γ.

The value of γ is determined from measured values of the specific heat of the sample versus temperature. The total specific heat of a metal can be written as

$$C_{\text{tot}}=\gamma T+\beta T^3\,,$$

where the second term on the right gives the Debye approximation to the low-temperature lattice specific heat. Data are plotted as (C_{tot}/T) versus T^2 in the usual manner, and γ is determined from the intercept of the resulting straight-line fit and the (C_{tot}/T) axis. The Debye temperature Θ is determined from the slope of the line.

Five samples were prepared with electron per atom ratios of 5.2 to 5.6 to take advantage of the strong dependence of the electron specific heat on $\mathfrak{z}$. The specific heats of these samples were measured as described above. The raw data are shown in Fig. 2. To demonstrate consistency, the data shown for the $VH_{0.5}$ sample are a composite of data from two experiments performed on separate occasions. The low-temperature deviation from linearity for data from the $V_{0.8}Cr_{0.2}H_{0.1}$ and $V_{0.6}Cr_{0.4}$ samples is not explained but may be due to residual adsorbed helium gas being driven from the sample. Because of this deviation, the straight-line fit to the data was determined principally from extrapolation of data taken above 2.5°K. The values of the electron specific-heat coefficient γ obtained from the (C_{tot}/T) axis intercepts of the data are shown in Table I and illustrated in Fig. 3. The least-squares method was used to fit the data. The metal hydride electron specific-heat coefficients are plotted in Fig. 3, assuming the hydrogen electrons were contributed to the metal conduction band. Then for

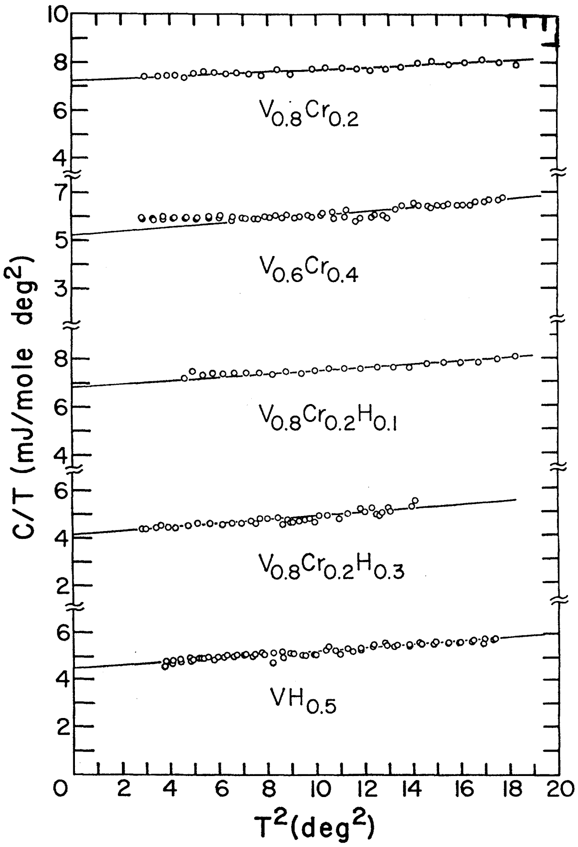

FIG. 2. Specific-heat data. Data on two separate experimental runs are shown for $VH_{0.5}$.

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[10] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

any alloy hydride $\mathfrak{z}=5+x+y$. Even though small corrections common to all the samples were not made, the absolute values of the measured electron specific heats of the $V_{0.8}Cr_{0.2}$ and $V_{0.6}Cr_{0.4}$ samples are in good agreement with published values.

At no time during the measurement of the specific heats of the five samples was there any evidence of a superconducting transition.

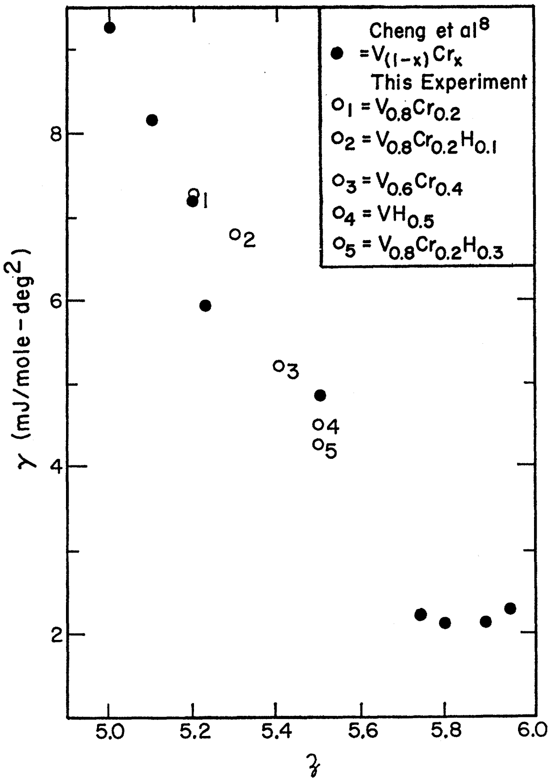

FIG. 3. Electron specific-heat coefficient versus electron-per-atom ratio. Solid circles represent data by Cheng (Ref. 8). Open circles are data from this paper. The strong dependence of the specific heat γ on $\mathfrak{z}$ is evident. The data for the V-Cr and V-Cr-H alloy systems depend on $\mathfrak{z}$ only.

At low temperatures $T\ll\Theta$, the Debye temperature Θ can be estimated using the following expression:

$$C_V=1944(T/\Theta)^3 \text{ J/mole °K}.$$

Using this approximation and the data shown in Fig. 2, the Debye temperatures were calculated for the alloys and metal hydrides. These values are shown in Table I with published values of the Debye temperature for vanadium metal and $V_{0.5}Cr_{0.5}$.

Due to the strong dependence of γ with $\mathfrak{z}$ as displayed in Fig. 3 for V-Cr alloys, one would expect the hydrided metals to have larger or smaller values of γ if the hydrogen atom, respectively, removed or added an electron to the metal conduction band. All metal-hydride samples displayed a definite decrease in the value of γ compared to the value of γ for the unhydrided metals. With the assumption of a contributed hydrogen electron, one might expect the $VH_{0.5}$ sample to have an electron specific-heat coefficient similar to that of $V_{0.5}Cr_{0.5}$ ($\mathfrak{z}=5.5$ for both). From the data available for V-Cr alloys, this value is 4.8×10^{-3} J/mole °K². The measured value of γ for $VH_{0.5}$ is within 15% of this value. This similarity should not be viewed as evidence that vanadium hydride and vanadium chromium have identical band structures, but should serve to indicate the effect of the hydrogen on the vanadium. The dependence on γ on the amount of alloying elements, whether they are Cr or H, lends heavy support to the idea that a hydrogen atom contributes its electron to the host transition-metal conduction band.

TABLE I. Specific-heat parameters γ and Θ for vanadium alloys.

Sample	Specific heat γ (mJ/mole °K²)	Debye Θ (°K)
$V_{0.8}Cr_{0.2}$	7.34±0.10	378±10
$V_{0.8}Cr_{0.2}H_{0.1}$	6.8 ±0.15	300±10
$V_{0.8}Cr_{0.2}H_{0.3}$	4.15±0.10	297±10
$V_{0.6}Cr_{0.4}$	5.2 ±0.15	286±10
$VH_{0.5}$	4.55±0.10	293±10
V[a]	9.25	380
$V_{0.5}Cr_{0.5}$[b]	4.85	314

[a] F. Heiniger, E. Bucher, and J. Muller, Phys. Kondersierten Materie **5**, 243 (1966).

[b] Reference 8.

IV. CONCLUSIONS

All metal hydride samples examined were found to have a definite decrease in the value of γ compared to the unhydrided samples. The values of γ for $V_{0.8}Cr_{0.2}H_{0.1}$ and $V_{0.8}Cr_{0.2}H_{0.3}$, for instance, are less than the value of γ for $V_{0.8}Cr_{0.2}$. In fact, the plotted points of the three alloy hydrides fall very close to the curve of γ versus $\mathfrak{z}$ for the V-Cr system when the assumption of the positive hydrogen ion is made.

This similarity would indicate that the rigid-band model is a useful approximating device for interpreting the effects of hydriding on the transition metals.

The fact that γ depends principally on the amount of alloying elements (the value of $\mathfrak{z}$) and not upon the relative amounts of chromium or hydrogen gives strong support to the concept that the hydrogen atom contributes its electron to the host transition-metal conduction band.

ACKNOWLEDGMENT

The authors thank Allen Garroway for his aid in many phases of this experiment.