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# A Simple Microcomputer-controlled Calorimeter: the Heat Capacity of Copper, Invar and $RbNiCl_3$ in the Range 2–20 K*

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*Abstract*

A simple inexpensive microcomputer has been used to control an adiabatic pulse-type calorimeter. The data acquisition control system incorporates a Rockwell AIM65 microcomputer to control all aspects of the thermometry and the injection of the heat pulse into the sample. Details of the hardware and software requirements are discussed, including the interface of the system with a host computer that uses the UNIX operating system. The performance of the apparatus was evaluated by measuring the heat capacity of 1965 Calorimetry Conference copper between 2 and 20 K. The results show a total r.m.s. deviation of less than 0·4% and agree well with the copper reference equation (r.m.s. deviation 0·4%). Measurements are also presented of the heat capacity of Invar (Nilo 36) and $RbNiCl_3$ over the same temperature range. In the case of $RbNiCl_3$ the heat capacity anomaly associated with the paramagnetic–antiferromagnetic transition is observed at 11·1 K.

## 1. Introduction

Computer automated calorimeters (Martin *et al.* 1973; Schwall *et al.* 1975; Joseph *et al.* 1976; Moses *et al.* 1977; Gmelin and Rodhammer 1981; Lanchester and Baker 1981; Cheung *et al.* 1982) currently fall into two main categories. They either incorporate expensive minicomputers with sophisticated hardware and software requirements (Martin *et al.* 1973; Schwall *et al.* 1975; Moses *et al.* 1977; Gmelin and Rodhammer 1981), or rely on microprocessors with their high development cost (Cheung *et al.* 1982).

The present paper describes an automated calorimeter that falls between these extremes, using a microcomputer to control the experiment and to transfer experimental data to a host computer for reduction. Advantages of this system are that it uses an inexpensive microcomputer that interfaces simply with digital voltmeters (DVMs) etc., requires no special computer programming expertise, communicates without elaborate interfaces to any computer network using a UNIX operating system, and has a high degree of operational flexibility as it may operate either as a stand-alone system or in conjunction with an existing computer system. The microcomputer operates the calorimeter in the adiabatic (or pulse) mode (Moody and Rhodes 1963). The performance of the apparatus is evaluated by heat capacity measurements on a sample of the 1965 Calorimetry Conference copper. New measurements are also presented on Invar and $RbNiCl_3$. The heat capacity of the latter shows a well defined

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cusp at 11·1 K where three-dimensional antiferromagnetic ordering occurs (see e.g. Rayne *et al.* 1981).

The present paper deals primarily with the automation of the calorimeter, as the subject of cryostat design and construction is well covered in the literature (White 1979).

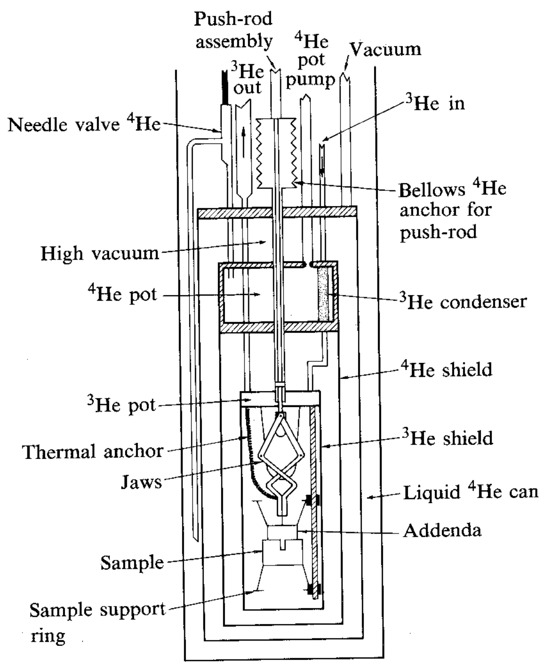


**Fig. 1.** Schematic diagram of the cryostat.

## 2. The Calorimeter

The calorimeter was designed to measure the heat capacity of solid samples between 0·3 and 30 K, but currently the range is limited by thermometer calibration from 2 to 20 K. It is of conventional design, using a $^3$He–$^4$He immersion cryostat (Scurlock and Wray 1965; White 1979; R. Hill, personal communication 1980), incorporating a heat switch with mechanical jaws to cool the sample. A schema of the cryostat is given in Fig. 1.

The temperature of the sample is measured using a germanium resistance thermometer (GRT), and subsidiary carbon thermometers are mounted on the $^3$He pot, $^4$He pot and shields. The sample is screwed onto the addenda which contain the GRT and a 4470 Ω heater, bifilar wound from No. 44B&S Evanohm wire. The addenda are suspended by fine nylon threads. Any stray heat input from external sources is minimized by mounting the cryostat/dewar system on an air cushion and 'sand-box' anti-vibration mounts. Anti-vibration couplings are used on all vacuum pumping lines.

## 3. Data Acquisition and Control System

*Hardware*

Fig. 2 is a schema of the data acquisition and control system. Only the novel and more significant features will be discussed; details such as electronic circuits are available from the author on request.

The main elements of the data acquisition and control system are the GRT supply and its associated Yokogawa DVM, timer/heat pulse unit and Fluke DVM combination to control the injection of the heat pulse into the sample, and the Rockwell AIM65 microcomputer combined with the binary-coded-decimal (BCD) interface for overall control and data management. All data transfers between the AIM65 and the various instruments in the data acquisition system use parallel BCD data interfaces with standard TTL logic.

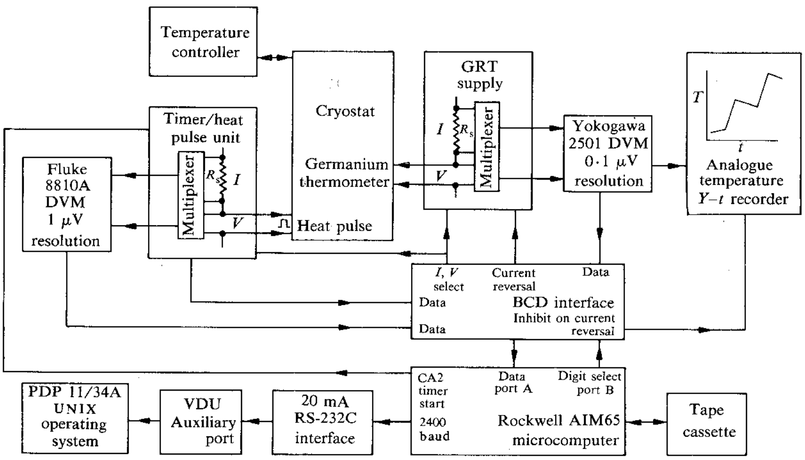


**Fig. 2.** Schematic diagram of data acquisition and control system.

The GRT supply consists of a current source, standard resistors and a multiplexer to switch the input of the DVM from the GRT to the standard resistor, or vice versa. The current source uses a high-precision voltage reference (Analog Devices AD581K) and a series of metal film resistors to provide 30 current ranges between 0·1 and 200 $\mu$A. The multiplexer is composed of low-thermal relays (Cato-Coil Company, Rhode Island, U.S.A.), which have a thermal offset rating of 200 nV per switch. In the interest of simplicity the computer only controls the multiplexer and a current reversal switch made from a quad bilateral switch (CD4066). Other functions are adjusted manually as required.

The timer/heat pulse unit is based on an Intersil 4 Digit CMOS up/down counter, type ICM7217, which is wired as a timer. The output from the timer is fed to a BCD counter, which on the count of four terminates the timing operation. The use of the timer, BCD counter combination and a 40 Hz timebase results in a timer that has a range from 0 to 999·9 s with 0·1 s resolution, generates a single time interval to control the current source, and informs the computer of the interval's duration and progression. This enables the heater current at the quarter and three-quarter points, and the heater voltage at the half-way point, to be measured. A quad bilateral switch (CD4066) is used as a multiplexer on the Fluke DVM input. The current source is made from an Analog Devices Precision Voltage source, AD584K, and metal film resistors, to provide a range of heater currents between 10 $\mu$A and 1 mA in 3 dB power steps. The AD584K has a strobe terminal, and is operated directly by the timer logic, eliminating the need for a relay to switch the current. Advantages include very fast switching ($<5$ $\mu$s), and hence a highly accurate pulse length, and added reliability. Both the timer/heat pulse unit and GRT supply use separate power supplies for the control logic and current source, thereby minimizing electrical interference effects. Optical couplers are employed on all computer control lines to eliminate ground-loop problems.

Data from the digital outputs of the DVMs and timer/heat pulse unit are fed into the AIM65 via the BCD interface. The interface, combined with the AIM65 two 8-bit user ports, functions as a 24 BCD digit multiplexer, and is made from cascaded SN74150 and SN74151 integrated circuits. The data are multiplexed one digit at a time into port A, with port B addressing the digit required. The three most significant bits of port B are used for control purposes, such as inhibiting the DVMs during data transfers, operating the analogue multiplexers and controlling the current-reversing switch in the GRT supply. The CA2 output from the AIM65 controls the start of the timer. The only hardware requirements for interfacing the AIM65 to a host computer are the conversion of the teletype 20 mA current-loop output to RS-232C, and a VDU with an auxiliary port.

```
grab.C
#include <ggtty.h>
main()
{
struct ggttyb vdu;
unsigned save;
int      c;
int      nchar;
char     inpchar;
gtty(0, &vdu);
save = vdu.mode;
vdu.mode |= RAW;
gtty(0, &vdu);
write(2,'OK\n',3);
while ( inpchar != '&') {
        nchar = read (0, &inpchar, 1);
        if ( inpchar < 0177 ) write(1,&inpchar, nchar);
        }
vdu.mode = save;
stty(0, &vdu);
}
```

**Fig. 3.** Program in C language for UNIX operating system to accept data from AIM65.

*Software*

Two programs are used. The first allows the AIM65 to control the experiment and acquire data from the various instruments. The other program forms part of the UNIX operating system on the host computer network which receives data from the AIM65.

The AIM65 control program is written in BASIC, except for a short machine language section which allows TIMER 1 to act as a clock to pace the measurements. The program is structured so that the calorimeter can be run in a continuous mode, measuring drift rates and injecting a heat pulse when the drift rate reaches an acceptable level, or in a step mode where the operator controls the injection of the heat pulse. The BASIC commands PEEK and POKE control the calorimeter and the acquisition of data via the BCD interface and user ports.

Two short programs transfer data from the AIM65 to the UNIX operating system. The first is a machine language program on the AIM65 to keep its keyboard active whilst data are transferred from the teletype port. The second (given in Fig. 3) is written in the C programming language (Kernigham and Ritchie 1978), and creates a new command called GRAB as part of the UNIX operating system. The GRAB command is quite general and can be used as a means of transferring data from any RS-232C compatible device to a UNIX based operating system.

## 4. Heat Capacity of Copper

The heat capacity of the 1965 Calorimetry Conference copper (Osborne *et al.* 1967) was measured between 2 and 20 K using a GRT calibrated on the EPT76 temperature scale (Kemp 1979) by the CSIRO Division of Applied Physics Temperature Measurement Group. The sample weighed 78·981 g and had the designation 'T6·1'.

At very low temperatures ($T \to 0$ K) the heat capacity of a non-magnetic solid varies with temperature as

$$C_p = \sum_{j=0}^{n} A_j T^{2j+1} . \tag{1}$$

The leading term in $T$ arises from the conduction electrons and the coefficient $A_1$ yields the limiting value $\Theta_0$ of the Debye temperature as $T \to 0$ K (see e.g. Barron and Morrison 1957). The higher order terms represent the effects of dispersion in the lattice spectrum, the discrete atomic structure of the solid, etc. The values of the electronic contribution and Debye temperature deduced from equation (1) are the same for $n \geqslant 4$, but the higher order terms are retained so that the polynomial can be used as an interpolation equation over the entire temperature range.

The heat capacity of the copper sample plus addenda (GRT, heater, copper support etc.) was measured, then the addenda alone. The addenda heat capacity was least-squares fitted (points weighted by $C_p^{-1}$) to equation (1) using orthogonal polynomials to produce an interpolating polynomial to correct the total heat capacity for the addenda contribution. An eighth-order polynomial yielded an r.m.s. deviation of 0·63%, and all systematic trends appeared to have been removed from the residuals. The addenda contributed about 18% of the total heat capacity.

The copper data were fitted to a fifth-order polynomial of the form (1) with an r.m.s. deviation of 0·4%. In Table 1 the coefficients of the polynomial with their standard errors are compared with those found by three other groups of workers.

The electronic heat capacity and the Debye temperature were estimated from the leading coefficients of the fifth-order polynomial. This yielded a value of 691·6±1·8 $\mu$J mol$^{-1}$ K$^{-2}$ for the electronic contribution and a Debye temperature of 344·5± 0·6 K.

The copper data found in the present work and those of three other groups of authors are presented in Fig. 4 as percentage deviations from the copper reference equation. It is obvious from Fig. 4 that the maximum deviation from the copper

**Table 1. Present coefficients $A_j$ of the polynomial (1) for copper compared with other results**
Standard errors are in parentheses; units of $A_j$ are $mJ\,mol^{-1}\,K^{-(2j+2)}$

| Coefficient | Present work | Copper reference equation[A] | Martin *et al.* (1973) | Hurley and Gerstein (1974) | Holste *et al.* (1972) Vacuum annealed | Holste *et al.* (1972) As received |
|---|---|---|---|---|---|---|
| $A_0$ | 0·69165 (0·00178) | 0·69434 | 0·7004 | 0·69142 | 0·69260 | 0·69466 |
| $A_1$ | 0·047533 (0·000225) | 0·047548 | 0·047055 | 0·047807 | 0·047369 | 0·047528 |
| $10^6 A_2$ | 11·6690 (5·8883) | 1·6314 | 8·6462 | 2·9721 | 1·9537 | 1·8155 |
| $10^8 A_3$ | −0·66838 (5·2188) | 9·4786 | 6·7646 | 8·9189 | 10·869 | 10·843 |
| $10^{10} A_4$ | 2·2374 (1·8065) | −1·3639 | −1·0386 | −1·3563 | −1·9745 | −2·0153 |
| $10^{14} A_5$ | −36·313 (21·114) | 5·3898 | 4·61297 | 5·7469 | 13·343 | 14·338 |
| $10^{17} A_6$ | | | −0·52698 | | −3·2196 | −3·8022 |

[A] See Osborne *et al.* (1967).

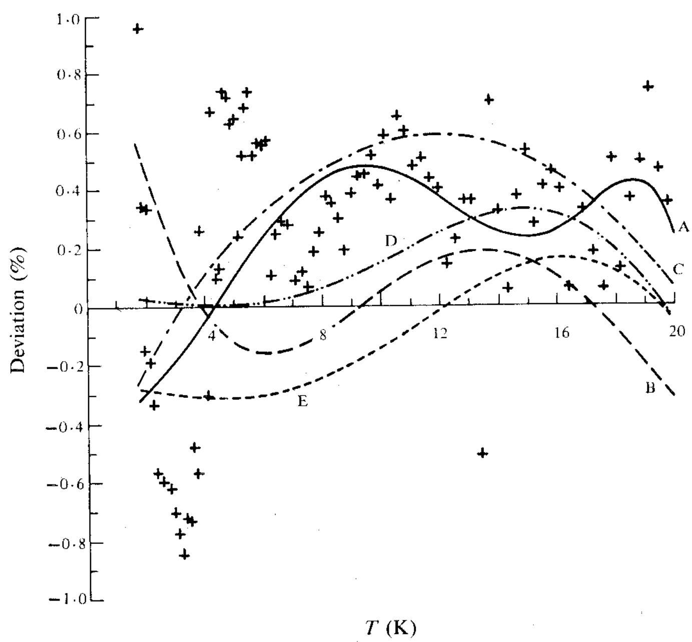


**Fig. 4.** Deviations of results from the copper reference equation for various workers, showing raw points (pluses) and smoothed curve A for the present work, results by Martin *et al.* (1973) (curve B), Hurley and Gerstein (1974) (curve C), and Holste *et al.* (1972) as received (curve D) and vacuum annealed (curve E).

reference equation is $-0\cdot3\%$ to $+0\cdot6\%$ for all workers with a general tendency to be slightly high. The discrepancies can arise because of different temperature scales, vacuum treatment of the copper sample, GRT calibration equations or systematic errors from heat leaks.

In the present case the heat capacity data were analysed in terms of the EPT76 temperature scale, whereas the copper reference equation is based on the NBS provisional scale 2–20 (1965). Holste *et al.* (1972) have examined the effect of temperature-scale differences on heat-capacity measurements, and concluded that a difference of 5 mK between two temperature scales would introduce a $0\cdot5\%$ discrepancy in $C_p$ at 1 K. For the case of the EPT76 and NBS 2–20 temperature scales, deviations of order $+0\cdot1\%$ to $+0\cdot2\%$ are to be expected below 4 K. At temperatures above about 10 K the major source of difference will be departure from thermodynamic smoothness or variations in the size of the degree.

It has also been observed that the value obtained for the heat capacity of copper is dependent on whether the sample is vacuum annealed prior to measurement (Martin 1967; Holste *et al.* 1972). The 'as received condition' yields a higher value for the heat capacity than the vacuum annealed condition (see Fig. 4, curves D and E). In the present case the sample was in the 'as received' condition and the results agree most closely with those of other workers whose samples were untreated.

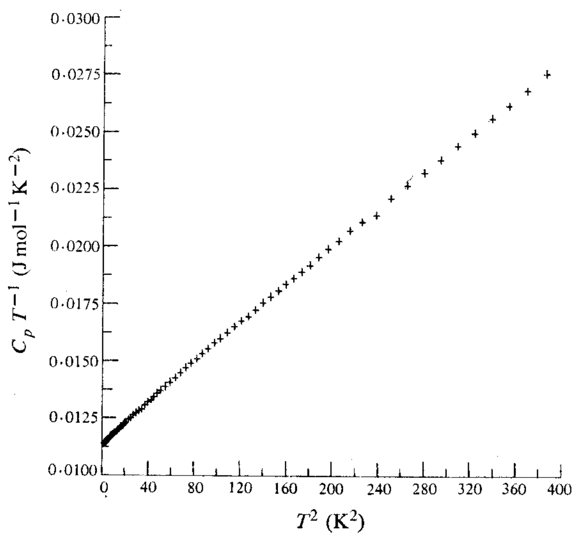


**Fig. 5.** Plot of $C_p\,T^{-1}$ against $T^2$ for Invar.

## 5. Heat Capacity of Invar and $RbNiCl_3$

*Invar (Nilo 36)*

There has been interest in this laboratory in the negative (magnetic) contribution to thermal expansion at low temperatures of iron–nickel alloys close to the Invar composition (see e.g. Barron *et al.* 1980). According to simple theory for magnetic alloys of the Invar type, both the magnetic and electronic contributions are linear in temperature, and thus not readily separable (see Barron *et al.* 1980). To complement existing thermal expansion data, the heat capacity of a $157\cdot047$ g sample of Invar ($Fe_{64}Ni_{36}$) has been measured between $1\cdot7$ and 20 K.

The results for Invar are shown in Fig. 5 as a plot of $C_p T^{-1}$ against $T^2$. This shows the electronic/magnetic and lattice contributions to the heat capacity. The data were fitted to a fifth-order polynomial of the form used for copper, with an r.m.s. deviation of 0·18%. The electronic/magnetic heat capacity and Debye temperature were deduced from the leading coefficients of the polynomial, yielding $(11 \cdot 27 \pm 0 \cdot 01) \times 10^{-3}$ $\mathrm{J\,mol^{-1}\,K^{-2}}$ and $336 \pm 1$ K respectively. Hausch (1975) obtained a value of 350 K for the Debye temperature from low temperature elastic measurements of an Fe–35% Ni alloy.

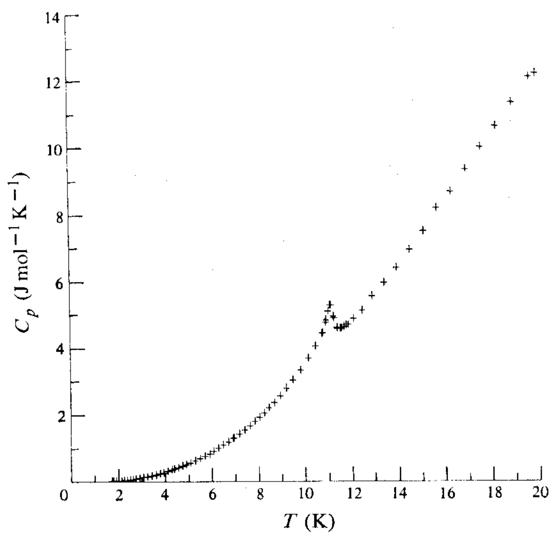


**Fig. 6.** Plot of $C_p$ against $T$ for $\mathrm{RbNiCl_3}$.

*$\mathrm{RbNiCl_3}$*

The compound $\mathrm{RbNiCl_3}$ is hexagonal and of type $\mathrm{ABCl_3}$ (A ≡ monovalent cation and B ≡ divalent transition metal ion) with a one-dimensional magnetic lattice (de Jongh and Miedeme 1974). The thermal expansion has been studied in this laboratory at temperatures from 2 to 90 K as part of an investigation of one- and three-dimensional magnetic ordering (Rayne *et al.* 1981).

A number of $\mathrm{RbNiCl_3}$ single crystals (total mass 7·5255 g) were attached to the addenda with Apiezon N grease. The heat capacity was measured between 2 and 20 K, with the addenda and Apiezon N grease contributing approximately 20% and 1% respectively to the measured heat capacity at 5 K. The results shown in Fig. 6 (corrected for addenda) as a plot of $C_p$ against $T$ show clearly the magnetic phase transition at 11·1 K.

## 6. Conclusions

The results obtained for the 1965 Calorimetry Conference copper, Invar and $\mathrm{RbNiCl_3}$ give confidence in the microcomputer-controlled calorimeter, proving its convenience and versatility of operation in obtaining heat capacity data for solids whose thermophysical properties show wide variation.

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