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SOME HEAT CAPACITY AND THERMOMETRIC INVESTIGATIONS AT ULTRALOW TEMPERATURES

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This research would not have been possible without sophisticated machinery for attaining and maintaining low temperatures. The author's contribution was not mainly in the construction of this machinery. Rather, this was the achievement of his co-workers P. M. Berglund, G. J. Ehnholm, R. G. Gylling, T. Heikkilä, M. Krusius and G. R. Pickett . The contribution of M. I. Aalto in designing and constructing the electronics of the pulsed NMR thermometer, employed in the latter part of this work, was invaluable. To the persons mentioned I should like to express my sincere thanks, as well as to all other laboratory personnel for their help throughout the experiments.

The author obtained a first introduction to nuclear orientation work during his visit to Clarendon Laboratory in Spring 1967.

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SUMMARY

This thesis consists of the following papers:

1. H. K. Collan, M. Krusius, and G. R. Pickett, ”Suppression of the nuclear heat capacity in bismuth metal by very slow spin-lattice relaxation and a new value for the electronic specific heat”, Phys. Rev. Letters *23*, 11 (1969)

2. H. K. Collan, T. Heikkilä, M. Krusius, and G. R. Pickett, ”On the measurement of small heat capacities at low temperatures”, Cryogenics *10*, 389 (1970)

3. H. K. Collan, M. Krusius, and G. R. Pickett, ”Specific Heat of Antimony and Bismuth between 0.03 and 0.8 K”, Phys. Rev. B*1*, 2888 (1970)

4. H. K. Collan, P. E. Gregers-Hansen, M. Krusius, and G. R. Pickett, ”Quadrupole Interactions in the Semimetals, As, Sb, and Bi”, *Proc. 12th International Conference on Low Temperature Physics*, E. Kanda, ed. (Keigaku Publishing Co, Tokyo 1971), p. 537

5. P. M. Berglund, H. K. Collan, G. J. Ehnholm, R. G. Gylling, and O. V. Lounasmaa, ”The Design and Use of Nuclear Orientation Thermometers Employing ^{54}Mn and ^{60}Co Nuclei in Ferromagnetic Hosts”, Report TKK-F-A155 (1971), to be published in Journal of Low Temperature Physics

6. M. I. Aalto, P. M. Berglund, H. K. Collan, G. J. Ehnholm, R. G. Gylling, M. Krusius, and G. R. Pickett, ”Construction and Use of a Pulsed Copper Nuclear Magnetic Resonance Thermometer”, Report TKK-F-A156 (1971), to be published in Cryogenics

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The interactions between the nuclear magnetic moment and the magnetic hyperfine (hf) field acting on the nucleus, and between the nuclear electric quadrupole moment and the electric field gradient at the site of the nucleus lead to hf energy levels. The splittings between these levels are in general measurable with high accuracy, for example by nuclear magnetic resonance (NMR) and by nuclear quadrupole resonance (NQR).

The nuclear heat capacity is caused by changes in the populations of the hf levels with temperature and measures only a weighted average of the hf interaction energy, but not the splittings themselves. With no further knowledge it does not give detailed information about the hyperfine interaction, especially because heat capacity work essentially relies on measurement of the absolute temperature and small temperature increments. Since the form of the hf Hamiltonian is often known from other considerations, measuring the nuclear heat capacity, nevertheless, provides an important independent possibility for checking the results obtained by resonance techniques.

The first paper reports results of a measurement of the specific heat of bismuth metal. In bismuth the hf energy is due to the coupling between the nuclear quadrupole moment and the electric field gradient resulting from the noncubic symmetry of the lattice. Prior to this work two contradictory determinations of the quadrupole coupling constant e^2qQ existed, one done by NMR and the other by a nuclear heat capacity measurement. Our work was aimed at resolving this discrepancy. Paradoxically, we could assign no value at all to the coupling constant, because it was found that the nuclear spin-lattice relaxation was too slow for establishing thermal equilibrium between the nuclear system and the lattice. This result provided strong evidence that the earlier heat capacity determination was erroneous. Assuming that the Korringa relation is valid, a lower limit of the Korringa constant was estimated to be 100 sK. Because of the decoupling of the hf thermal reservoir from the lattice, we could separate the electronic heat capacity more accurately than earlier. The new value was significantly smaller than earlier determinations.

The main experimental difficulty in the work of the first paper was due to the unexpectedly small heat capacity. The common nearly adiabatic principle of heat capacity determination was abandoned, and a more accurate method taking into account the energy exchange between the sample and the surroundings was employed. The author's independent contribution was to work out the method, and to carry out a full analysis of the experimental data. He also took part in all other aspects of the work.

The measurement of small heat capacities in non-adiabatic conditions is dealt with in more detail in *the second paper*. The three co-authors gave only minor contributions.

The third paper reports results of a specific heat determination of the semimetal antimony. The results of the bismuth measurement of the first paper are also further discussed. The higher conduction electron density of antimony gives rise to a larger electronic heat capacity and a faster relaxation between the nuclear spin system and the lattice than in bismuth. Now the hf energy contributes fully to the total heat capacity, and an accurate calorimetric determination of e^2qQ is possible. A nearly adiabatic technique of measurement was possible because the total heat capacity was large. The results were in accordance with an earlier NQR measurement and, in the high temperature range of the present work, with several other heat capacity determinations. The author participated in all sides of the experimental work of this measurement.

In the first paper it was suggested that the nuclear heat capacity of bismuth could be made visible by doping a bismuth sample with tellurium. Results of the heat capacity measurement of doped bismuth are reported in *the fourth paper* confirming this prediction and the earlier NMR determination of e^2qQ. The magnitude of e^2qQ was found to depend more strongly on alloying than anticipated. Apart from the suggestion of the doped bismuth measurement the author's contribution to the new results of the fourth paper was nominal.

In the heat capacity work the temperature scale was based on a downwards extrapolation of the ^{3}He vapour pressure scale with the aid of the susceptibility of cerous magnesium nitrate (CMN). At the low temperature end of the measurements the temperature determination accuracy was thus limited by the non-ideal paramagnetic behaviour of interacting magnetic moments. In order to determine accurately even lower temperatures, a system with smaller internal interactions than a paramagnetic salt is preferable. A good choice is a nuclear spin system where the ordering temperature arising from dipole-dipole interactions between spins is several orders of magnitude lower than with electronic spins.

The fifth paper deals with absolute temperature measurement by employing dilute radioactive impurity nuclei imbedded into a ferromagnetic metal lattice. The hf Hamiltonian governing the polarization of these nuclei is well known. The degree of polarization can be determined by observing the anisotropic γ-radiation emitted by the nuclei. The magnitude of the hf splitting has been determined earlier for a number of combinations of impurity nuclei and host metals, and is of the order of 10 mK for the cases considered. Therefore, by nuclear orientation (NO) techniques the standard temperature scale can be established at around 10 mK. This is important as recently the lowest experimental thermal equilibrium conditions have been pushed down to 0.5 mK by nuclear spin refrigeration. The advantages of NO thermometry do not, however, seem to have been generally appreciated, partly because of the instrumental corrections needed in practical work. In this paper we show that these corrections do not present insurmountable difficulties. The low temperatures, down to 2 mK, necessary for this work were obtained by employing the nuclear refrigerating cryostat of this laboratory. NO thermometry was used simultaneously with a pulsed copper NMR thermometer; it was concluded that at about 10 mK the absolute temperature can be determined with 2% accuracy, removing the necessity of long extrapolations when calibrating thermometers for work below 10 mK. The author took care of the design of the NO system and of the analysis of the relevant data.

Ultralow temperature thermometry is further investigated in *the sixth paper*. CMN thermometry and NMR thermometry on one hand, and NMR and NO thermometry on the other are compared with each other. A pulsed copper NMR thermometer was found to be an easy to manage and accurate thermometer below about 0.5 K. The author participated in the experimental work of the latter part of these experiments and in the analysis of the results. These results give, a posteriori, additional evidence that the temperature scale used in the heat capacity work of this thesis has indeed been well founded.