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A FARADAY MAGNETOMETER FOR THE MEASUREMENT OF SMALL LIQUID-QUENCHED ALLOY SAMPLES

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Abstract: A Faraday magnetometer which is currently used for measuring magnetic susceptibility (χ) of small liquid-quenched Al alloys in the region 1.5—300 K is described and details of calibration procedures are given. Provided that suitable precautions are taken to minimize unwanted forces and that proper correction is made for any feromagnetic contamination, it is possible to measure χ with a total specimen mass of 20 mg to an absolute accuracy of 1 % and to resolve changes of $2 \cdot 10^{-10}$ emu/g.

1. Introduction

Detailed studies of the magnetic susceptibility χ of aluminium based 3d alloys and some other alloys with a high Kondo temperature are difficult to perform because:

- the contribution to χ from the 3 d element is small, typically 10^{-6} — 10^{-7} emu/gm/at. % and practically temperature independent, and
- using normal methods of quenching from the melt often less than 0.1 at % of the 3d element can be retained in solid solution.

Although there are several ultra-rapid quenching (URQ) techniques which provide large enhancement of the solid solubilities for a number of alloy systems, the samples obtained are usually very small. Recently, using a new technique in which the molten alloy is quenched between rapidly rotating rollers[1] it has been possible to obtain longer samples suitable for measurements of electrical resistivity[2] and thermoelectric power[3]. Since the dimensions of these samples are typically 10 mm × 2 mm × 20 μm they are still rather small for susceptibility measurements, but by making up a bundle of such samples with a total mass of 20 mg or so we can measure χ (T) to a relative accuracy of about 1 in 10^3 over the temperature range 1.5 — 300 K.

In this paper we describe the experimental methods used and give examples of the results obtained. The apparatus was set up for studying Al-3d alloys, especially Al-Mn and Al-Cr, and up to now was used for investigations both with regard to the Kondo effect and the effect of magnetic interactions between the 3d atoms in these alloys. The same apparatus may be used in the future for investigations of weakly magnetic systems such as other Kondo alloys, thin metallic films and some of the »one dimensional« organic conductors which are currently of interest. It may also be of use for metallurgical investigations on the URQ Al alloys.

The Faraday method is used to measure χ; the force exerted on the sample by an inhomogeneous magnetic field is measured using a commercially available electrobalance (Cahn model RG 2050). Because we are using such small samples it is necessary to obtain the maximum sensitivity of the balance when mounted above the cryostat. This arrangement is discussed in Section 2. In Section 3 sample suspension is described and the unwanted thermomolecular and magnetic forces on the suspension are dicussed. The calibration and testing of the apparatus are dealt with in Sections 4 and 5.

Finally, in Section 6 details of the sample preparation and corrections for ferromagnetic contamination are given, and the results for an URQ Al sample are compared with those in the literature.

2. *Balance: mounting and sensitivity*

In order to minimize vibrational noise the balance is rigidly mounted in a laboratory on the ground floor of the building. The arrangement used is shown schematically in Fig. 1. Two sets of split aluminium plates B hold the glass vacuum vessel containing the balance and are fixed to a thick steel plate C, which is in turn bolted to the main frame A constructed from heavy steel girders and bolted to the concrete floor. The electromagnet is normally supported on the same frame and can be rolled out on tracks perpendicular to the plane of the diagram, thus allowing the metal dewar D to be lowered (against the counterweights E) when changing specimens. The vertical position of the magnet can be adjusted with the hydraulic jack F.

With this arrangement the sensitivity of the balance in situ was well within the value of 0.1 μg stated by the manufacturer. When the balance and sample chamber were under vacuum with a total load (sample plus suspension) of 500 mg, and a one second time constant, the peak to peak noise was 0.1 μg. Apparently it would be rather difficult to improve on this figure since it is only a factor of 10 or so larger than the limit to the resolution of beam balances due to Brownian motion as discussed by Poulis[4]).

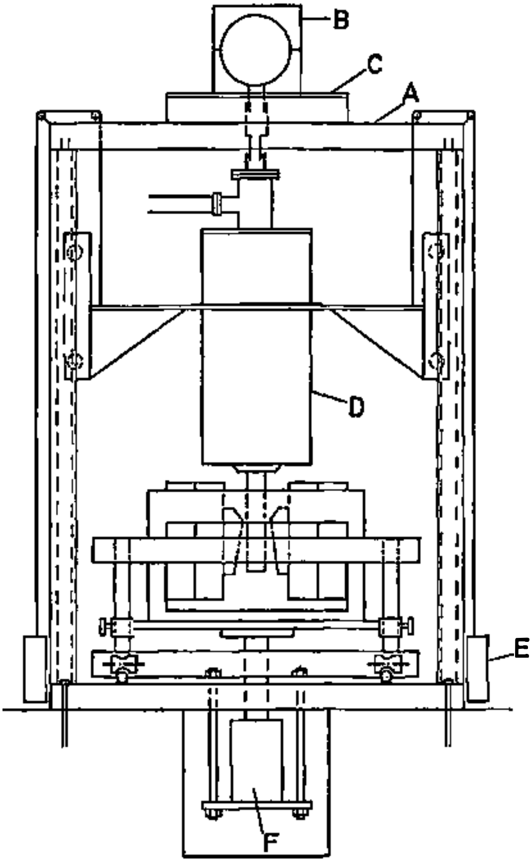

Fig. 1. Overall view of the apparatus (schematic) *A*-main support frame, *B*-split Aluminium plates, *C*-thick steel plate, *D*-metal Helium dewar, *E*-counter weights, *F*-hydraulic jack.

3. *Suspension*

Description. A diagram of the sample suspension and calibration mechanism is given in Fig. 2. The suspension itself is made by hooking together 3 fine quartz (fused silica) fibres each 0.2 mm in diameter and 30 cm long. A 4 mm diameter quartz sphere fused on to the middle link keeps the suspension under tension and also supports an aluminium foil radiation shield. One possible improvement would be to mount this sphere halfway down the lowest fibre, thus increasing the lateral stability (Section 5), while still keeping the sphere sufficiently out of the field to minimize the »empty holder« force.

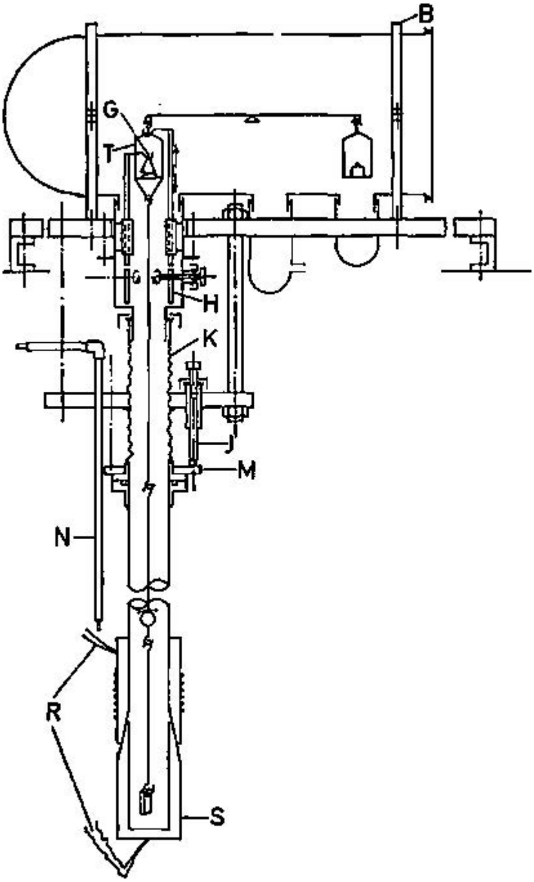

Fig. 2. The suspension and calibration mechanism (not to scale). *G*-calibration weight, *H*-eccentric cam, *K*-stainless steel bellows, *J*-alignment screw, *M*-pressure plate, *N*. Helium transfer siphon, 0-heater, *R*-Thermocouples, *S*-copper sample chamber and sample *s*.

The upper quartz fiber is hooked on the stirrup *T*, which also supports a pan made of aluminium foil, and *s* is then hooked on to the balance arm. During a run the calibration of the balance is checked periodically by lowering the 765 μg calibration weight *G* on the Al pan. When the eccentric cam *H* is rotated through the vacuum seal the calibration weight is smoothly raised and lowered by a brass rod. A similar arrangement is used on the opposite side of the stirrup to disconnect the suspension from the balance arm when changing samples. The cupronickel down tube shown in Fig. 2 is connected to the top of the cryostat by a flexible stainless steel bellows *K*. Thus by tightening the three screws *J* (only one is shown in the figure) against the pressure plate *M*, the down tube can be made accurately vertical[5]. It is then easy to align it with the narrow tail of the dewar and there is less possibility of the sample or suspension rubbing against the long down tube. By the use of the copper cone joint shown in Fig. 2 specimens can be changed easily. Because of superfluid leaks in this joint, there were some difficulties with the measurements below the He λ-point and continuous pumping on the sample chamber was necessary. Even then the noise level of the balance was a factor of 10 higher than usual.

Weakly magnetic samples are hung directly on the quartz hook as shown, while more strongly magnetic ones have to be held in a quartz bucket to avoid lateral instabilities.

Unwanted forces on the suspension. Blank runs were performed to enable the magnetic force on the suspension, the »empty holder« force, to be subtracted. In the maximum magnetic field the force on the quartz bucket was too large, $\cong 2$ dynes, so it could not be used with the URQ Al samples. They were hooked directly on the lower quartz fibre where the magnetic force was $\cong 5 \cdot 10^{-3}$ dynes i. e. 1/20 of a typical sample force. Within the accuracy of our measurements it was independent of temperature below 77 K.

Apart from having a small temperature independent diamagnetism, quartz is good material for the suspension because of its extremely low coefficient of thermal expansion[6]. Change in the sample position on cooling down due to the contraction of the suspension should be less than 0.1 mm.

Usually in this sort of apparatus He exchange gas is admitted into the sample chamber to a pressure of several torr to provide thermal contact between the sample and the copper cap on which the thermometer and heater are mounted. This gives rise to another unwanted force — the thermomolecular force (TMF) on the suspension. Although it is straightforward to allow for the TMF by subtracting successive readings with and without an applied field, nevertheless it must be kept small in order to reduce zero drift during measurements and to use the most sensitive range of the balance. We investigated the performance of our apparatus at different He exchange gas pressures from $5 \cdot 10^{-3}$ to 5 torr, with the sample chamber at 4.2 and 100 K.

For both sample chamber temperatures the TMF reached a maximum value of 0.3 dynes around 1 torr. However at 4.2 K the noise level of the balance also increased as with pressure, as has also been observed by others[7]. It was not detected at 100 K and at room temperature so it can possibly be attributed to the onset of thermal oscillations in the enclosed He gas[8]. Therefore with regard to sensitivity and low TMF, at 4.2 K pressure should be less than 0.02 torr. The test described in the following section showed that for our apparatus, which has a long narrow down tube and a radiation shield on the suspension, such a pressure provided adequate thermal contact between the specimen and the copper cap.

4. Temperature measurement and calibration

Below 4.2 K the sample temperature is determined from the vapour pressure of the pumped He bath controlled with a mercury manostat. Temperatures above 4.2 K, are obtained by boiling off the liquid helium until it falls below the copper cap, can be controlled to some extent by varying the power of the heater on the cap. Two Au 0.03 at% Fe-Chromel thermocouples are used to measure the temperature of the copper cap. One has its reference junction in the He inside the dewar and is used from 4.2 — 40 K. The other one with its reference junction at 0°C outside the dewar, is used from 40 — 300 K. Thermocouple voltages are measured to the nearest μ V using a 6 digit digital voltmeter, which is also used to measure the output from the balance. Thermocouples made from the same reel of Au Fe wire were calibrated by one of us several years ago. The voltage measured with one junction in ice and the other at 4.2 K (4640 μV) agreed with the previous calibration to within 10 μV and to this accuracy has not changed over a period of one year. This indicated that the previous calibration is valid for our thermocouples as was confirmed by the results given below for a AuGd alloy.

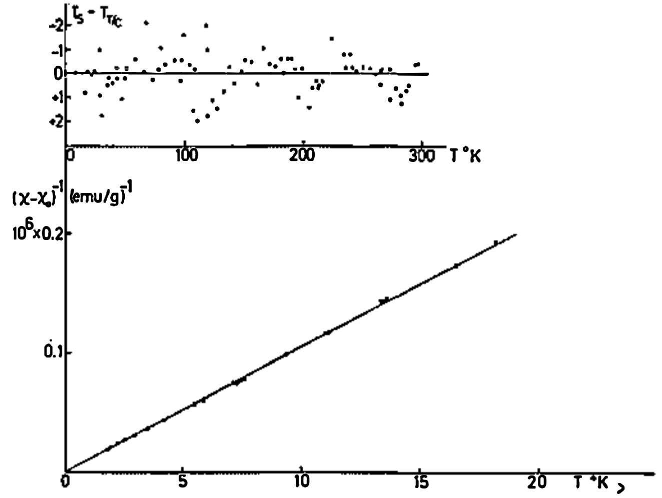

Fig. 3. Results for a Au 0.3 at% Gd specimen. Upper plot: Sample-thermocouple temperature diference ($T_S - T_{T/C}$) versus temperature indicated by thermocouple ($T_{T/C}$). The sample temperature T_S is obtained from the equation $\chi - \chi_{Au} = 98.5 \,.\, 10^{-6}/T_S$ emu/g which fits the data near room temperature. χ_{Au} is taken to be — 0.14 · 10emu/g[13].

Lower plot: $(\chi - \chi_{Au})^{-1}$ vs $T\,(K)$ showing the accuracy of the sample temperature determination in the low temperature region. The straight line corresponds to the above equation.

We made further tests to ensure that with the He exchange gas pressure normally used (0.015 torr at 4.2 K rising to 0.06 torr at 77 K) there was satisfactory thermal contact between the samples and the thermocouples. This was done by measuring the susceptibility of a Au 0.3 at. % Gd alloy, which is known to obey Curie law to an accuracy of about 0.05 K down to 1.5 K[9]. Our results are shown in Fig.3. The low temperature results show that any steady temperature difference between the sample and the thermocouple due to heat conduction or radiation down the tube is less than 0.1 K. Together with the results at higher temperatures they also confirm the thermocouple calibration.

TABLE

SUSCEPTIBILITY OF SOME STANDARD SAMPLES AT ROOM TEMPERATURE
$T = 293 — 297$ K

Sample and purity	Measured	Literature	Produced by
	10^{-8} emu/g		
Pd	(524)	524 ± 3[13)]	Supplied with Cahn electrobalance
Al (4N5)	60.8 ± 0.2	60.4 ± 0.4[10)]	Johnson-Matthey »Specpure« Aluminium
Cu (5N)	-8.55 ± 0.02	$-8{,}60 \pm 0.03$[11)]	»Asarco« copper

A second test was made to measure the thermal lag between the specimen and the thermocouples. For the AuGd specimen the readings obtained under almost static conditions were compared with those obtained when the temperature of the copper cap was increasing at known rate. It was found that the sample-thermocouple equilibrium time was of the order of 10 s at 10 K and 150 s around room temperature. Therefore a small temperature drift during measurement could be tolerated, and usually sufficient stability could be achieved by manually adjusting the heater power to the copper cap.

5. *Measurement of* χ

Determination of the field gradient. An electromagnet (Alpha Scientific Inc. model 9500) with specially shaped »constant force« pole pieces (13 cm in diameter) and a gap of 4 cm provides a large and uniform field gradient. The gradient $\frac{HdH}{dz}$ was plotted out versus the x, y (horizontal) and z (vertical) co-ordinates by measuring the force on a small Ti cylinder, 5 mm long and 1 mm in diameter, which was suspended directly on the quartz hook, for different positions of the magnet. The resulting field profiles are shown in Fig. 4, the optimum sample position is at the maximum of $\frac{HdH}{dz}$ in the z direction and at the minima for the horizontal directions. These field profiles are also useful for estimating possible errors arising both from errors in positioning the sample and from using samples of different dimensions. The magnitude of $\frac{HdH}{dz}$ at the optimum position was obtained primarily by measuring the force on a Pd cylinder, 1 cm long and 2 mm in diameter, supplied with the Cahn balance and using the value of χ given in the Table. Two sets of measurements were made in the first the specimen was held in a quartz bucket and in the second it was suspended directly from the quartz hook. For the latter there were problems due to lateral instability at fields of 6 kG and above, but at lower fields both methods gave the same values for $\frac{HdH}{dz}$. Some other standard specimens were also measured at room temperature and their susceptibilities were calculated on the basis of the Pd calibration. For these specimens the M (H) curves were linear within the experimental error, i. e. there was no detectable saturating component to the magnetisation (see Section 6). The good agreement with the results in the literature shown in the Table indicates that the calibration at maximum field is accurate to ± 0.5%. Furthermore, the linearity of the M (H) plots obtained both for the standard samples and some unquenched Al alloys shows that the relative values of $\frac{HdH}{dz}$ at other fields are also accurate to this level. The maximum value of $\frac{HdH}{dz}$ is $11.35 \cdot 10^{6}$ gauss^{2} cm^{-1}.

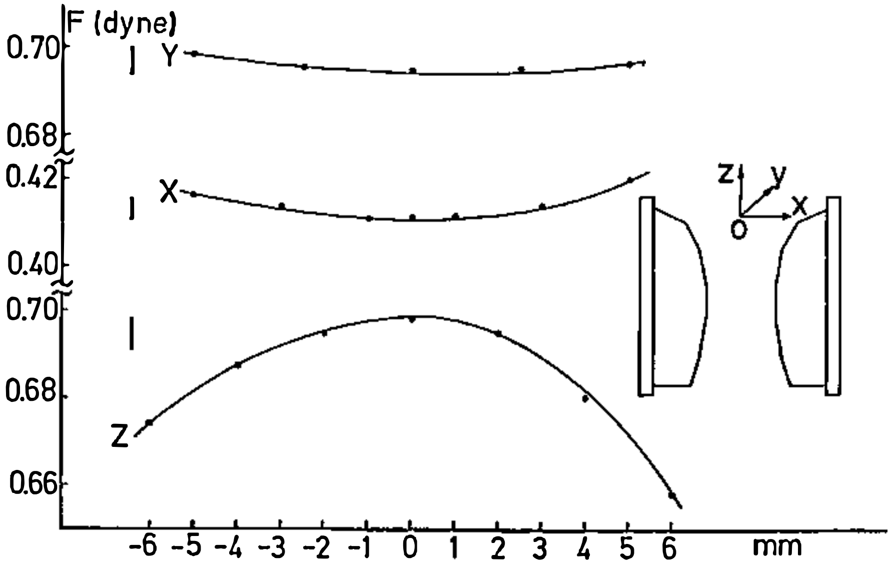

Fig. 4. Plots of magnetic Force $\left(\text{i. e. } H\frac{dH}{dz}\right)$ versus specimen position for a small Ti sample.

Determination of the magnetic field. In order to obtain a large force on the specimen the magnetic field H is necessarily inhomogeneous and changes by 13%/cm in the sample region, so it is not easy to measure H precisely. We used a small (3mm × 4 mm) auxiliary InSb Hall probe to measure H for different magnet currents and immediately calibrated it against a temperature compensated Bruker Hall probe in an homogeneous field. The latter probe is used in nuclear magnetic resonance work and was known to be sufficiently accurate for our purpose. The gradient $\frac{HdH}{dz}$ determined from the force measurements on Pd was accurately proportional to H^{2}, where H was determined with the Hall probe. For fields between

3 and 9.4 kG (the maximum obtained) we found that the ratio $\frac{H\mathrm{d}H}{\mathrm{d}z}/H^2$ equals $0.128_5 \pm 0.001\ \mathrm{cm}^{-1}$ i. e. there is very little change in the field distribution in this range. These observations show that, although the absolute accuracy of the field determination is at most a few per cent because of the inhomogeneity, the relative accuracy and reproducibility for various values of the magnet current is better than 1%.

Tests of lateral stability. If the sample is correctly positioned in the x and y directions (see Fig. 2) then by symmetry, the horizontal magnetic force is zero. However, for large enough field gradients the sample is unstable with respect to displacements in the x direction. This »lateral instability« occurs when the horizontal magnetic force at finite x tends to exceed the gravitational restoring force there. For full discussion the reader is referred to the work by Stewart[12]. These horizontal forces are proportional to the corresponding vertical magnetic F_M and gravitational forces F_W acting on the sample and suspension. So a criterion for lateral stability can be expressed in terms of F_M and F_W. For example, if the sample and suspension are represented by a simple pendulum of mass m and length l, then $F_W = mg$ and the stability criterion is approximately

$$F_M < mg\frac{G}{l}.$$

The quantity G has dimension of length and is related to the spatial variation of the magnetic field. We have not measured G directly for our magnet, but for an order of magnitude discussion we can take $G \cong 5$ cm. An upper limit to G is the quantity $H/\frac{\mathrm{d}H}{\mathrm{d}z}$ which we determined to be 8 cm.

We tested the lateral stability of our system by using two paramagnetic samarium samples of different masses (40 and 20 mg) and found values of 2 and 1 dyne respectively for the maximum vertical force F_{MC}. These values are not very accurate because the instability points were not sharply defined. At forces a factor of two lower the specimens had already moved out by 1 mm. The latter values represent upper limits to F_M.

Both the magnitude of F_{MC} and the proportionality with the sample mass are consistent with the formula given by Stewart for a hinged suspension. Despite the fact that F_W is roughly constant, since the 73 mg suspension is considerably heavier than the Sm samples, the sample mass enters in the stability criterion because in our present arrangement it determines the mass (or moment of inertia) of the lowest link. The final theoretical criterion obtained for our suspension is given by equation with m representing the sample mass and l the total length of the suspension (100 cm).

We conclude that the lateral stability of the magnetometer is well understood. For specimens suspended directly on the quartz hook and meausred in maximum field a practical upper limit to χ (corresponding to a horizontal diplacemnet of 1 mm) is $3 \cdot 10^{-6}$ emu/g independently of the mass of the sample. This is adequate since for a 20 mg sample it is 10^4 times the resolution of the apparatus. More strongly samples must be held in the 400 mg quartz bucket and with this F_M can be as large as 15 dynes.

6. *Measurements on Al alloys*

Sample preparation. The preparation of the URQ Al alloys has already been described elsewhere[1]. We took some additional precautions because of the possibility of contamination by Fe or other small ferromagnetic particles. The master alloys were chemically cleaned just before quenching and the quenched samples were washed in dilute nitric acid, distilled water and alcohol. The URQ samples were handled with stainless steel tweezers and trimmed to shape using a glass cutting tool. For $\chi(T)$ measurements a rectangular bundle of dimensions 5 mm × 2 mm × 1 mm was formed from 30—50 samples of thickness 20 — 40 μm. A longer sample was wrapped around the bundle to hold it together and the end of this sample was bent over and hooked on to the suspension of the balance. During mounting and precooling the samples were at room temperature for about four hours.

Ferromagnetic contamination. Despite the above precautions a small amount of ferromagnetic contamination has been detected in all the quenched samples measured up to now. The contamination is introduced during the rapid quenching process or when assembling the bundle of samples afterwards. For an Al 0.4 at % Cu alloy which was measured before quenching there was no detectable contamination (i. e. less than 0.05 ppm of free Fe particles), whereas after quenching the same sample had a ferromagnetic component corresponding to a weight of 1.6 ppm of free Fe particles. This was a typical value for most of the URQ samples measured.

As a result of this contamination, instead of being straight lines through the origin the magnetization curves contain a saturating part $\Delta(H)$ i. e.

$$M(H) = \Delta(H) + \chi H.$$

In the worst cases, for example for the URQ pure Al sample referred to in the following section, Δ could be 20% of χH at the maximum field and an even larger fraction at lower fields. However since Δ was saturated by fields of about 3 kilogauss, χ could be obtained from the slope of a straight line fit to $M(H)$ at higher fields.

The fitting procedure (or the equivalent one actually used) increases the random error in χ, but the uncertainty can be minimized if the values of the gradient $H \frac{\mathrm{d}H}{\mathrm{d}z}$ and the field H, at different magnet currents, are known to a high relative accuracy, as described in Section 5.

In practice we used the equivalent Honda-Owen fitting procedure and plotted M/H (i. e. the apparent susceptibility at a given field) versus $1/H$ for fields from 4 to 9.4 kilogauss. Straight lines, showing Δ to be saturated, were invariably obtained and the correct value of χ was given by the intercept at $1/H = 0$. In general the Honda-Owen plots at different temperatures were parallel within the experimental error. Thus the saturating value of Δ was independent of temperature and it was only necessary to subtract a small constant term from the values of χ measured at a certain field.

Some caution must be exercised in interpreting the Honda-Owen plots at low temperatures where a change in slope does not necessarily mean that the saturating value of Δ has changed — it could be due to the onset of Brillouin curvature in the magnetisation curve.

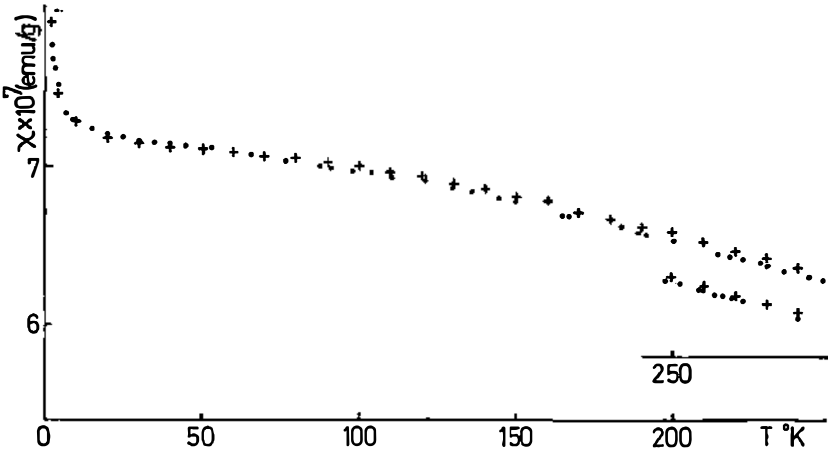

Fig. 5. Comparison of our $\chi(T)$ results for an URQ Al specimen (●) with those of Hedgcock and Li (+)$^{10)}$.

Results for URQ pure Al. Our results for a series of Al-3d alloys will be submitted for publication elsewhere. As an example of the results obtained, in Fig. 5 is shown a comparison of our measurements on an URQ Al sample (4N7 Al mass 37 mg) with those of Hedgcock and Li$^{1\,2)}$ for a sample prepared in the normal manner. The results are in good agreement although there are small discrepancies above 100 K. It is thought that these represent real differences between the URQ and the normally quenched Al samples rather than measurement errors. Our results for several quenched and unquenched Al alloys show that for all the URQ samples the change in χ between 100 and 150 K is a little larger than for equivalent unquenched samples. This effect is not understood but may arise from distortions or defects of the lattice introduced by rapid quenching.

This particular sample was one of the first to be measured and the saturating component Δ was 3 times larger than usual. Nevertheless, Δ was independent of T and the values of χ obtained from the Honda-Owen plots are in agreement with the results in Ref.$^{1)}$, where the value of Δ was negligibly small.

7. *Conclusion*

We have described the construction and calibration of a Faraday magnetometer for measuring small URQ alloy samples, which has a resolution of $2 \cdot 10^{-10}$ emu/g for a 20 mg sample, and have given examples of its performance. By paying attention to the mounting of the balance, the minimization of unwanted thermomolecular and magnetic forces on the sample suspension, and making appropriate corrections for ferromagnetic contamination, it is possible to measure $\chi(T)$ for these small samples as accurately as for conventional ones. For the previous year the apparatus has been used successfully for measurements of URQ Al-3d alloys in relation to the Kondo effect.

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UREĐAJ ZA MJERENJE MAGNETSKE SUSCEPTIBILNOSTI FARADAYEVOM METODOM MALIH ULTRA-BRZO KALJENIH UZORAKA

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Sadržaj

Opisan je uređaj za mjerenje magnetske susceptibilnosti Faradeyevom metodom u temperaturnom području od 1.5 — 300 K koji se koristi za male uzorke aluminijevih legura dobivenih kaljenjem iz tekuće faze.

Osjetljivost uređaja za uzorke mase 20 mg je $2 \cdot 10^{-10}$ emu/g. Ovako velika osjetljivost uz malu masu uzorka i slabo magnetsko polje rezultat je uklanjanja uzroka nestabilnosti vage (vibracije zgrade, termomolekularna sila) i smanjenja doprinosa neželjenih sila. Po apsolutnom iznosu susceptibilnost je određena do na 1 %

U temperaturnom području od 4.2 — 300 K temperatura je mjerena termočlankom Au 0.03 at% Fe-Chromel a od 1.5—4.2 K mjerenjem tlaka para tekućeg He^4.

Da bi se usporedila temperatura kalorimetra koja se mjeri termočlankom i temperatura uzorka izmjerena je susceptibilnost legure Au 0.3 at% Gd za koju je poznato da slijedi Curieovo ponašanje od 300 — 1.5 K. Također je mjereno vrijeme potrebno da uzorak poprimi temperaturu kalorimetra. Na kraju mjerena je susceptibilnost čistog aluminija koja se vrlo dobro slaže sa rezultatima iz literature.