Zeitschrift: Helvetica Physica Acta
Band: 41 (1968)
Heft: 6-7

Artikel: Anomalous low temperature specific heat of alloys near the critical concentration for ferromagnetism
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DOI: https://doi.org/10.5169/seals-113940

Schluss

Für Legierungen mit normalen Metallen hat man durch die geschilderten Untersuchungen eine gute Möglichkeit, die Theorie von FABER und ZIMAN zu bestätigen. Für Legierungen mit Übergangs- und seltenen Erdmetallen kann man die Erweiterung der Theorie von FABER und ZIMAN auf diese Legierungen prüfen und dann wichtige Schlüsse über die Elektronenstruktur dieser reinen flüssigen Metalle, je nach Lage von K_p und $2\,k_F$, ziehen.

Unser Dank gilt Herrn Prof. Dr. G. BUSCH für seine Anregung zur Untersuchung der Elektronenstruktur flüssiger Metalle und Legierungen, für seine Ideen, die den Fortschritt auf diesem Gebiet stark beeinflussen, und für sein grosses Interesse, das er unseren Arbeiten entgegenbringt.

Wir danken auch den Herren H. SEILER und O. STEIGER für die während ihren Diplomarbeiten ausgeführten Messungen.

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Anomalous Low Temperature Specific Heat of Alloys near the Critical Concentration for Ferromagnetism

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(29. IV. 68)

Abstract. The specific heat of an alloy 63% Ni, 37% Rh has been found experimentally to have an anomaly at low temperatures [8]. This anomaly has so far been interpreted in terms of *d*-electron-paramagnon interactions. An alternative interpretation, given here, is based on the superparamagnetic behaviour of very small ferromagnetic particles, envisaged to be clusters which are rich in nickel. Under reasonable conditions of particle size, anisotropy etc., the anomalous contribution to the specific heat is a constant independent of temperature and determined by the number of clusters in the alloy. The experimental data fit this constant term very well and using also magnetic data on an alloy with the same concentration [7], it is shown that very roughly 10% of the alloy must be contained in clusters for the anomaly to be explicable in this way. The anisotropy is tentatively suggested to be surface anisotropy. A table is also given comparing the anomalous specific heat of this alloy with the anomalies observed previously in a wide range of other alloy systems.

1. Introduction

For normal metals and alloys at low temperatures the specific heat is given by the formula

$$C = \gamma T + b T^3, \tag{1}$$

where the first term represents the electron and the second term the phonon contribution. For a wide range of alloys with compositions near the critical concentration for ferromagnetism (see §2) it has, however, been observed that the experimental data need for their representation an additional term, i.e.

$$C = A(T) + \gamma T + b T^3. \tag{2}$$

If, as is customary, the experimental data are plotted as C/T against T^2, the anomalous term then appears as $A(T)/T$, and on this plot it is shown as an upturn at low temperatures.

The present paper is concerned with the origins of this anomaly. Apart from nuclear contributions to $A(T)$ there are two possible causes which have been discussed. The first is related to superparamagnetic effects due to atomic clustering or fluctuations in composition [1–3]. In the simplest approach [2] $A(T)$ was shown to be a constant but there are more complicated results elsewhere [3] and the theory of this effect is discussed in §4. The second approach relates $A(T)$ to the many body effects [4–6] involved in the interactions between electrons and spin waves (magnons) or persistent spin fluctuations (paramagnons). A brief account of this subject is given in §3.

It is concluded that, on considering both the theoretical and the experimental situation, it is at least as likely that the anomaly arises from superparamagnetic effects as from the more fundamental effects related to many body interactions.

In a companion paper COTTET et al. [7] report and consider other measurements on nickelrhodium alloys which is also the central alloy system with which the present paper is concerned.

2. Experimental Facts

The impetus to the present work was given by the specific heat measurements of BUCHER et al. on Ni-Rh alloys [8]. The anomaly was clearly observed and the temperature independent value of A deduced from their measurements (see §4) is given in Table 1. These authors interpreted the anomaly by means of the many body effects referred to in §3. The fit with the prevalent law $A(T) \sim (T/T_s)^3 \ln (T/T_s)$ is, however, very imperfect over the wide temperature range covered. This could be due to theoretical reasons leading to the inapplicability of the law in detail. As shown in §4, however, the fit to a constant A, arising from the simplest form of superparamagnetic theory gives very reasonable results as do the deductions made from the actual values of A for Ni-Rh and other alloy systems.

Such constant values of this function $A(T)$ had been used for many years to fit the specific heat anomalies of a wide range of alloys. Among alloy systems studied and exhibiting this effect are those listed in Table 1 (see also [18]), which gives the value of the temperature independent specific heat anomaly term A in each case. The entries in this Table show that there are some irregular variations among the smaller A

values [11], that the largest A values frequently occur near critical concentrations for ferromagnetism, that A is sensitive to metallurgical treatment and that A for the Ni-Rh alloy is very much in line with the other entries.

Table 1

Temperature independent specific heat anomaly

Alloy	A (m J deg^{-1} mole^{-1})	Reference
63% Ni, 37% Rh	4.5	[8]
40.5% Ni, 59.5% Cu	5.5	[2, 9]
43% Ni, 57% Cu		[10]
As cast	2.6	
Homogenized	4.6	
Quenched	3.7	
45% Ni, 55% Cu	4.4	[11]
55% Ni, 45% Cu	1.1	[11]
74% Ni, 26% Zn	3.4	[11]
80% Ni, 20% Mn	0.9	[12]
75% Ni, 25% Mn different treatments	0.2–2.2	[12]
70% Ni, 30% Mn	1.2	[12]
60% Ni, 40% Mn	2.0	[12]
91% Ni, 9% V	3.0	[12]
82% Ni, 18% V	1.3	[12]
26% Fe, 74% V	8.0	[2, 13]
28% Fe, 72% V	9.9	[2, 13]
30% Fe, 70% V	2.8	[2, 13]
50% Fe, 50% Ti	9.0	[14]
50% Fe, 50% Al	13.9	[15]
65% Fe, 28% Ni, 7% C	2.6	[12]
dto., field cooled	2.4	[12]
4.5% Fe, 85.5% Cr, 10% Al	1.3	[16]
13.5% Fe, 76.5% Cr, 10% Al	6.4	[16]
27% Fe, 63% Cr, 10% Al	0.4	[16]
40% Pd, 60% Ag+75 ppm Fe	0.4	[17]
dto., cold worked	0.2	[17]
41% Pd, 59% Ag+35 ppm Fe	0.6	[17]
45% Pd, 55% Ag+105 ppm Fe	0.4	[17]

On the other hand, SCHINDLER and MACKLIET [19] (see also [20]) have reported no anomaly in a Ni-Pd alloy with 1.95% Ni, very close to the critical concentration (an anomaly was observed at about 1.1° K but this is thought to have a different origin). The absence of the effect here may be due either to fundamental [21] or to metallurgical reasons, for example that nickel and palladium form unusually good solid solutions with little clustering or statistical fluctuation effects.

3. Review of Fundamental Effects[1])

The many body effects leading to anomalous low temperature specific heats are concerned with the interactions between the *d*-electrons in transition metals close to the critical concentration for ferromagnetism and the persistent spin density fluctuations (paramagnons) whose lifetime increases to large values as the critical concentration is approached. The present theoretical treatment of these effects is based on the usual short range interaction model of magnetism in transition metals [22]. The Hamiltonian contains a single particle term

$$H_{sp} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}}\, a^*_{\boldsymbol{k}\sigma}\, a_{\boldsymbol{k}\sigma}\,, \tag{3}$$

where $\varepsilon_{\boldsymbol{k}}$ is the single particle energy, σ the spin and the a are creation and destruction operators. It also contains an interaction term

$$H_{int} = \frac{1}{2}\,\frac{I}{N} \sum_{\boldsymbol{q}\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} a^*_{\boldsymbol{k}+\boldsymbol{q}\sigma}\, a^*_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}\, a_{\boldsymbol{k}'\sigma'}\, a_{\boldsymbol{k}\sigma}\,, \tag{4}$$

where I is the effective interaction energy and N the number of atoms. The corresponding dynamic susceptibility in the random phase approximation is given by

$$\chi(\boldsymbol{q}, \omega) = \chi^0(\boldsymbol{q}, \omega)/\{1 - I\,\chi^0(\boldsymbol{q}, \omega)\}\,, \tag{5}$$

$$\chi^0(\boldsymbol{q}, \omega) = \sum_{\boldsymbol{k}} (f_{\boldsymbol{k}} - f_{\boldsymbol{k}+\boldsymbol{q}})\,(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{\boldsymbol{k}} - \hbar\,\omega - i\,\delta)^{-1}\,, \tag{6}$$

where the $f_{\boldsymbol{k}}$ are Fermi functions and δ a small positive constant. The H_{int} term may be rewritten so as to contain terms of the form

$$-\frac{1}{2}\,\frac{I}{N} \sum_{\boldsymbol{k}\boldsymbol{q}} a^*_{\boldsymbol{k}+\boldsymbol{q}\downarrow}\, a_{\boldsymbol{k}\uparrow}\, \sigma^{(+)}_{-\boldsymbol{q}}\,, \tag{7}$$

where $\sigma^{(\pm)}_{\boldsymbol{q}}$ are the spin density fluctuation operators. The matrix elements for scattering of electrons from paramagnons corresponding to the transition $\boldsymbol{k}$ to $\boldsymbol{k} + \boldsymbol{q}$ involve [23] the spectral weight function $A(\boldsymbol{q}, \omega) = 2\,\Im\,\chi(\boldsymbol{q}, \omega)$ as given by (5) and (6). Thus it is possible to calculate the free energy and hence the specific heat. At low temperatures the two most important results of this calculation are [4]: (i). The linear term in the specific heat formula (2) is enhanced compared to the value derivable from one-electron theory.

(ii) $$A(T) \sim (T/T_s)^3 \ln(T/T_s)\,, \tag{8}$$

where $T_s \sim T_F\,(1 - I)$, with T_F the degeneracy temperature and $I = I\,N(\varepsilon_F)$ involving the single particle density of states at the Fermi energy. The critical concentration for ferromagnetism corresponds to $I \to 1$ and the anomaly is thus largest at concentrations close to critical. It was, however, shown [5] that the form (8) of the anomaly may only be applicable at exceedingly low temperatures; elsewhere it would then have to be obtained numerically. Unfortunately these results were not applied to the data on Ni-Rh alloys, where the theory might have been expected to apply.

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[1]) In preparing this section of the paper we have had much helpful advice from M. J. Rice.

Further, FULDE and LUTHER [24] have shown that for disordered alloys scattering effects serve to influence $A(T)$ so as to make it of the form

$$A(T) \sim (T/T_s)^3 \ln ((T + T_i)/T_s) . \tag{9}$$

Here T_i is characteristic of the scattering and may be appreciable enough compared with the measuring temperatures so as to make $A(T)$ no longer anomalous but practically indistinguishable from the T^3 term in (2)[2]).

A similar situation arises [21] if the enhancement of $\chi(\boldsymbol{q}, \omega)$ by the interaction I given in (5) is not a property of the whole crystal but is localized on nearly ferromagnetic impurities in a non-magnetic matrix. LEDERER and MILLS [21] envisage nickel impurities in palladium as an example. The spectral weight function $A(\boldsymbol{q}, \omega)$ then has two terms [25] and so finally has the specific heat. The specific heat contribution corresponding to the matrix, though still of the form (8), was then shown to be swamped by the contribution from the impurities which was shown to go as T^3. Hence the total effect is again an enhancement of the T^3 term in (2). The experimental evidence for such an effect is at present not wholly conclusive [19, 20].

Whereas [4] applies only to nearly ferromagnetic substances, BUCHER et al. [8] suggested that the many body effects proposed for this range of concentrations should also apply beyond the critical concentration ($\bar{I} > 1$), as long as the alloys are only weakly ferromagnetic. This situation is discussed in [5], [6] and [26]. We are, however, compelled to refute a number of assertions made in [6] where reference is made to the specific heat of Cu-Ni alloys and to the clustering interpretation of the anomalous results:

The linear specific heat coefficient γ in relation (2) was found to vary anomalously only for the copper rich Ni-Cu alloys. For pure nickel the value of γ obtained from energy band calculations and that observed differ by no more than about 50% [27], and this discrepancy can easily be accounted for as resulting from electron-phonon interactions. For the alloys with up to about 50% Cu the observed γ values are roughly constant [10], and this variation was accounted for reasonably well in [1]. The anomalously large γ values for alloys approaching and beyond the critical concentration as well as the $A(T)$ anomaly discussed here (see Table 1) were ascribed in [1] and [2] to clustering effects. Although not ruling out some contribution to γ near the critical concentration from the many body effects referred to above, it is interesting to not that GOLDMAN [28], on developing the clustering idea further, in fact managed to interpret the γ values even of copper-rich alloys on this basis. The present paper is concerned with $A(T)$ and the theoretical background of the anomaly based on the clustering idea is given in §4. We are, however, at a loss to understand what is meant in [6] by the statement '...an explanation of the specific heat of the Cu-Ni alloys in terms of ... clusters yields an unreasonable dependence of the *Debye* temperature on the nickel concentration'.

In this section we have tried to present the many body interpretation of the anomaly $A(T)$ as objectively as possible. All the evidence, however, points to the interpretation based on superparamagnetism, and described in §4, as being at least as

[2]) We understand from S. DONIACH that more recent investigations have revealed a change in the detailed functional form.

plausible, at least when applied to the Ni-Rh alloy of BUCHER et al. [8] given in Table 1.

4. Superparamagnetic Interpretation of the Anomalous Specific Heat and Other Data for Nickel-Rhodium

A theoretical discussion of the specific heat anomaly arising from superparamagnetism was given by SCHRÖDER [2] and LIVINGSTON and BEAN [3]. This discussion, which is summarized below refers in its simplest form to well defined small homogeneous ferromagnetic particles whose magnetization vectors fluctuate thermally with a characteristic relaxation time determined by the particle volume, the anisotropy energy, the magnitude of any applied magnetic field and the temperature, and reaching for very small particles, values less than the time of a measurement [29, 30]. These particles are envisaged as being distributed in a non-ferromagnetic matrix, e.g. iron in mercury, and, in the simplest form of the theory of superparamagnetism, no account is taken of magnetostatic interactions between the particles.

It seems, however, that the theory may well have rather wider applicability than is implied by these ideals. Thus, taking nickel-rhodium alloys near the critical concentration as an example, it is only necessary to envisage small slightly nickel rich regions to exist, for statistical or other reasons, in a slightly rhodium-rich matrix for the specific heat anomaly to have a good chance of manifesting itself in the way to be described.

The nickel-rhodium alloy of BUCHER et al. [8] appears to have a 'Curie temperature' about 40 °K as apparent from a peak in the susceptibility, temperature curve. A value very much of the same order of magnitude, about 60 °K, was also observed in [7] for a specimen with the same nominal composition 63% Ni, 37% Rh. This value was also obtained as the temperature of an anomalous change in the susceptibility, temperature plot. Reference [7], however, also leads to another estimate of an apparent 'Curie temperature' of only about 20 °K, this one from a plot of M^2 against H/M, where M is the magnetization (Arrott plot). However, it is by no means certain that this method of Curie point determination is at all reliable for the type of heterogeneous alloy being considered here; instead we believe that this lower temperature has no significance and that the rhodium-rich matrix can be regarded as essentially non-ferromagnetic. On the other hand, it is clear that the clusters envisaged will have a broad spectrum of sizes, Curie temperatures, magnetizations, anisotropies etc., so that no very close agreement between the simple theory outlined in [29], [30] and the magnetic and thermal data for the Ni-Rh alloy is to be expected. In fact, the agreement is rather better than one would have hoped for, as shown both here and in [7].

For most conceivable applications (but see below) the specific heat of superparamagnetic particles is given classically as

$$\left.\begin{aligned} A(T) &= \frac{\partial}{\partial T}\left\{k\,T^2\,\frac{\partial \ln Z}{\partial T}\right\}, \\ \text{where} \quad Z &= \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \exp\{-E_A(\phi,\theta)/kT\}\, d\theta \end{aligned}\right\} \qquad (10)$$

and $A(T)$ *here* refers to the specific heat of one particle. Also Z is the partition function and $E_A(\phi, \theta)$ the anisotropy energy as a function of the direction ϕ, θ of the magnetization. LIVINGSTON and BEAN [3] obtained $A(T)$ for the special cases of uniaxial anisotropy, $E_A = \pm v K \sin^2\theta$, where K is the ansotropy constant and v the particle volume. For unidirectional anisotropy (or interaction with an external field), $E_A \sim -\cos\theta$. They also considered the quantum mechanical case of low spin values S. The results of this calculation, together with a number of generalizations are most readily considered in terms of two characteristic temperatures T_A and t_A, such that

$$k\,T_A = E_A^0, \quad t_A = T_A/S. \tag{11}$$

Here E_A is a measure of the anisotropy energy, defined by $E_A^0 = \bar{E} - E_0$, where E_0 is the quantum mechanical ground state energy and $\bar{E}$, given by

$$\bar{E} = (2\,S+1)^{-1} \sum_{i=1}^{2S+1} E_i, \tag{12}$$

is the mean anisotropy energy, the E_i being the eigenvalues of the relevant anisotropy Hamiltonian [31]. For positive uniaxial anisotropy, for example, $E_A^0 = 2/3\,v\,K$.

For practical problems $S \gg 1$, i.e. $T_A \gg t_A$. There are then three different ranges of the temperature:

(1) $T < t_A$. Here quantum mechanical effects are responsible for the behaviour of $A(T)$; for $T \to 0$, $A(T)$ vanishes exponentially [3] as a result of the finite separation between the lower energy levels. Nernst's theorem is thus obeyed!

(2) $t_A \ll T \ll T_A$. Here the classical approach is appropriate and, from (10) and (11), assuming uniaxial anisotropy with a positive constant K, it was found that [3]

$$\left.\begin{aligned} A(T)/N\,k &= \frac{1}{2} - (e^{\beta}/4\,I)\,(1 - 2\,\beta + e^{\beta}/I), \\ \text{where} \qquad I &= \int_0^1 e^{\beta t^2}\,dt, \quad \beta = \frac{3}{2}\,(T_A/T), \end{aligned}\right\} \tag{13}$$

and N is the number of clusters. In the limit $T \ll T_A$, it may be shown that

$$\frac{A(T)}{N\,k} = 1 + \alpha\,\frac{T}{T_A} + O\left(\frac{T}{T_A}\right)^2, \tag{14}$$

where α is a numerical factor determined by the type of anisotropy; for positive uniaxial anisotropy, $\alpha = 2/3$. Relation (14) gives, in agreement with the equipartition principle and obtainable generally, a constant $A(T)$ at low temperatures as defined, this constant being determined by the number of clusters [2, 3]. For strictly uniaxial *negative* anisotropy, however, the first term on the right hand side of (14) becomes 1/2 [3].

The higher terms in (14) are also interesting, especially the linear term which adds to the electronic heat, as pointed out in [3].

(3) $T \gg T_A$. Using (13) it is easy to show that here

$$\frac{A(T)}{N\,k} = \frac{1}{5}\left(\frac{T_A}{T}\right)^2, \tag{15}$$

giving a decreasing specific heat contribution. It can be shown that this T^{-2} law is more general than is implied by the classical approach and the assumption of uniaxial anisotropy. In fact, in the same limit and for any value of S,

$$\frac{A(T)}{N k} = (\overline{E^2} - \overline{E}^2)/(k\,T)^2, \tag{16}$$

to lowest order, where $\overline{E}$ is given by (12) and $\overline{E^2}$ is defined in an obvious manner.

In order to apply these results to the specific case of the nickel-rhodium alloy of Table 1 it is necessary to have some information regarding the following parameters:

(1) Mean moment per cluster, leading to an estimate of the mean number of atoms per cluster.

(2) Anisotropy energy, leading to an estimate of the characteristic temperature T_A and hence, from (1), of t_A.

(3) Mean number of clusters per mole, N. If $T \ll T_A$ from (2) then $A(T)$ is nearly a constant as described, this being then an immediate measure of N. Hence from (1) the fraction of the alloy volume occupied by clusters, as compared with the rest which forms the matrix, may be determined.

In what follows these parameters are estimated, either directly from the value of A in Table 1, or from the magnetic measurements of [7], or from what are regarded as reasonable physical ideas. Although no great accuracy can be claimed for any of these estimates the analysis as a whole is intended to show once again the usefulness of the superparamagnetism concept in the description of alloy behaviour.

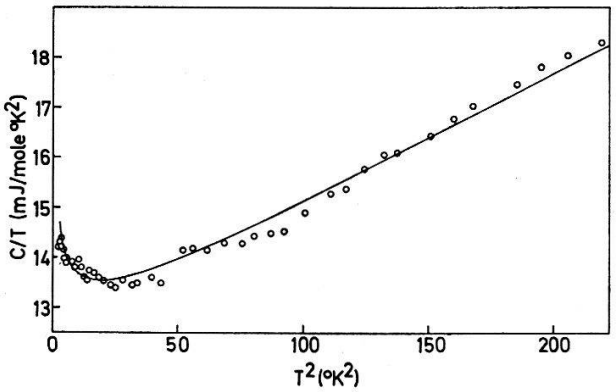
(1) The mean magnetic moment per cluster of alloys of this type may be estimated from magnetic measurements. VAN ELST et al. [32] used the standard analysis [29, 30] of magnetization isotherms to obtain values of 25 μ_B and 60 μ_B for nickel-copper alloys with 30 and 40% Ni, respectively. For these alloys there is, however, a *known* trend towards segregation into nickel and copper rich phases on a submicroscopic scale, as revealed by the neutron irradiation experiments of RYAN et al. [33]. No such experiments have yet been reported on nickel-rhodium alloys near the critical concentration. A similar analysis of Nevitt's magnetic [34] data on Ti-Fe, given in [14], yielded a moment per cluster of about 120 μ_B in that case. The magnetic data on the Ni-Rh alloy being discussed here are reported in [7]. An analysis of these data gives an estimate for the mean moment per cluster of about (200 $\pm$ 100) μ_B.

(2) A reliable estimate of the anisotropy energy E_A^0 of the clusters is clearly impossible since the origin of the anisotropy is unknown. In special cases, such as the Ni-Mn alloys of Table 1, the interaction between ferromagnetic and antiferromagnetic phases leads to the so-called exchange anisotropy [29, 35]. The magnitude of the effect may here be estimated from the shift of the hysteresis loop characteristic of the effect and from an assumed cluster moment of 100 μ_B similar to that found in other cases, giving for the Ni-Mn alloys of Reference [35] T_A values of several tens °K and t_A several tenths. There is no evidence of the presence of antiferromagnetic phases in Ni-Rh, so another effect must be sought. For the small, irregularly shaped clusters which are envisaged this could well be the so-called surface anisotropy first introduced by NÉEL [36]; see also [29], where the term 'internal surface anisotropy' is introduced which may well be particularly apt for our problem. Néel proposed that the leading part of the angle-dependent interaction energy of an array of parallel spins, with ϕ_{ij}

the angle between the magnetisation and the vector $\boldsymbol{r}_{ij}$ joining nearest neighbour spins, and with l a constant,

$$W = l \sum_{ij} \left(\cos^2 \phi_{ij} - \frac{1}{3} \right), \tag{17}$$

while vanishing for cubic symmetry, remains finite for a small particle with a surface deviating from cubic symmetry. Here the contributions to W from all bonds $\boldsymbol{r}_{ij}$ are no longer compensated. In a cluster containing of the order of 200 or so spins and correspondingly $N_b \sim$ some hundred bonds $\boldsymbol{r}_{ij}$, the number of uncompensated $\boldsymbol{r}_{ij}$ may be of the order $N_b^{1/2}$, i.e. roughly of order 20 or so. From this the anisotropy energy can be estimated to be of order 20 l. Taking values of l from typical magnetostriction values [29], p. 315, the temperatures T_A and t_A of Ni-Rh are found to be of the order of some tens and some tenths °K, respectively.



Plot of reduced specific heat C/T as a function of T^2 of the alloy 63% Ni, 37% Rh [8], and fit of the data to the relation (18).

Clearly these estimates can not be taken too seriously. A more realistic model of superparamagnetism in heterogeneous alloys will be based on a more unified view rather than the separate discussion of the anisotropy of ill defined clusters each having internal isotropic exchange interactions. On the other hand, the estimates of T_A and t_A are such that the measuring temperatures lie in the range where (14) is applicable. Hence the constant value of A in Ni-Rh is reasonably well explained.

(3) This constant value of A was obtained from the Ni-Rh measurements of [8], and the Figure shows a fit of these data, over the temperature range up to 15 °K, to the formula

$$\frac{C}{T} = \frac{A}{T} + \gamma + b\, T^2, \tag{18}$$

with $A = 4.5\ \mathrm{mJ\ deg^{-1}\ mole^{-1}}$, $\gamma = 12.0\ \mathrm{mJ\ deg^{-2}\ mole^{-1}}$, $\theta_D = 416\ ^\circ\mathrm{K}$. Note that this value of γ differs from that of [8], where $\gamma = 14.6\ \mathrm{mJ\ deg^{-2}\ mole^{-1}}$; hence the change of γ compared with pure nickel is now only about 70%.

From the value of A for this alloy the number of clusters per mole, N, may be obtained immediately from (14), giving N about 3×10^{20}. From this value, and the number of Bohr magnetons estimated above from the magnetic measurements [7] it follows that the fraction of the alloy which is distributed in clusters is about

$$\frac{4.5 \times 10^{-3} \times (200 \pm 100)}{8.3 \times v} \sim \frac{1}{v} (10 \pm 5)\ \%, \tag{19}$$

where v is the number of Bohr magnetons per cluster atom. The value of v can not be estimated but is presumably less than 1. Hence the final conclusion is that to interpret both the magnetic data and the specific heat anomaly a small but significant part of the alloy must be contained in clusters as discussed.

Whereas the whole of the specific heat anomaly has been ascribed to clustering effects, these give only a small contribution to the linear term in the specific heat on the basis of relation (14): From this and the values of A and γ only about 1% is obtained, if T_A is put equal to 40 °K and $\alpha \sim 1$. In other alloys the enhancement of γ due to these causes may, however, be larger.

Another possible source of a superparamagnetic contribution to the linear term is supplied by the low-temperature fall-off in the temperature range of t_A. The estimate of some tenths of a degree given above is obviously a rather rough one, and the possibility cannot be excluded that t_A may fall into the experimental range of temperatures of some degrees Kelvin for a fraction of the clusters at least. In this case, which was listed above as (1), the cluster specific heat contribution is no longer a constant but follows an Einstein specific heat function in the simplest approximation [2], t_A being the Einstein characteristic temperature. Obviously in this case, in fitting the experimental data to (2) with a constant A, part of the magnetic contribution will be absorbed into γ and b, γ being enhanced, b being lowered, and A no longer measuring exactly the number N of clusters according to (14) but only the order of magnitude of N.

Very small values of b and even negative ones were obtained by a least squares fit of the experimental data to relation (2), leading to unreasonably high or even negative values of the Debye temperature, when interpreted as a lattice specific heat contribution [11, 15, 16]. A consistent qualitative explanation for this behaviour seems possible along the lines given above. A quantitative estimate of the superparamagnetic contribution to γ seems impossible at present, but if the mean Einstein temperature should really happen to fall into the experimental range of temperatures of 1 to a few °K the superparamagnetic contributions to A and γT are expected to be of the same order of magnitude.

In any case a fairly conclusive experimental test of the validity of the superparamagnetic concept can be obtained by a systematic study of the magnetic field dependence of the specific heat of alloys of the type under consideration. The rough estimates of some tenths °K for t_A given above leads to an anisotropy field $H_A = k\,t_A/2\,\mu_B$ of a few kOe. An external magnetic field H of some 20 or 30 kOe applied during the specific heat measurement is appreciably larger and should thus essentially determine t_A. This would yield a shift of t_A to values larger by a factor 5 or 10, and thus a decrease of the superparamagnetic specific heat contribution according to the Einstein function.

As far as we are aware there has as yet been no systematic investigation of this field dependence over a range of field strengths[3]). Instead only three isolated experiments have been reported with a field applied during measurement [11, 12]. The results are listed in Table 2. The values of A, γ, and Debye temperature θ_D result from a least squares fit and are also taken from the original references. The field causes a drop of the lowest temperature specific heat in two of the three cases and an appreciable drop

[3]) More recently E. BUCHER has started such investigations on Ni-Rh.

Table 2

Variation of low temperature specific heat by an external magnetic field

Alloy[a]	H (kOe)	C (1.4 °K) (10^{-4} cal deg^{-1} mole^{-1})	A (10^{-4} cal deg^{-1} mole^{-1})	γ (10^{-4} cal deg^{-2} mole^{-1})	θ_D (°K)	Reference
$Ni_{0.48}Cu_{0.52}$	0	21.3	5.75	16.9	346	[1]
	14	18.8	4.15	15.6	321	
Ni_3Mn[b]	0	25.6	5.26	20.7	261	[12]
	14.5	24.7	3.80	21.5	266	
Ni_3Mn[c]	0	20.7	3.65	18.1	291	[12]
	14.5	21.0	3.14	18.3	316	

The units in Table 2 differ from those in Table 1 as the effect is more clearly shown up thereby.
[a]) In all cases the sample was cooled in a magnetic field H to 1.4 °K.
[b]) Quenched from 1100 °C.
[c]) Quenched from 1000 °C, annealed 2 hr. at 485 °C.

of A in any case, in accordance with expectation from an enhanced t_A and giving further evidence for the superparamagnetic explanation of the low temperature specific heat anomaly. This preliminary discussion strongly suggests a systematic experimental investigation of the field dependence of the lowest temperature specific heats in alloys of the type under consideration and in external fields H large compared to the anisotropy fields H_A[3]). As we have discussed, the experimental range of temperatures is then expected to be closer to t_A than to T_A. Hence the specific heat anomaly would be represented more closely by an Einstein function,

$$A(T) = N\,k(t_A/2\,T)^2/\sinh^2(t_A/2\,T)\,, \qquad k\,t_A = 2\,\mu_B\,H\,, \tag{20}$$

than by (14).

The present paper has been concerned in the main with the nickel-rhodium alloy made topical by Reference [8]. Clearly much additional information is required to show whether the clustering concept which we have advanced is at all reasonable. The companion paper [7] is concerned with measurements of static magnetic properties, some of which have been used here, as well as with electron paramagnetic resonance and velocity of sound studies of an alloy with the same nominal concentration. Again, a part of the discussion is based on the concept of clustering.

We are grateful to E. Bucher, M. J. Rice, C. P. Bean, J. D. Livingston, M. Peter, P. Donzé, E. Kneller, S. Doniach and E. Vogt for helpful discussion, and have great pleasure in dedicating this paper to Professor G. Busch on the occasion of his birthday.

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Untersuchung der kondensierten Materie mittels Neutronenstreuung

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Die Beobachtung der Streuung langsamer Neutronen an Festkörpern und an Flüssigkeiten stellt heute eine bedeutende Methode dar, um die Struktur und die Dynamik kondensierter Materie zu erforschen. Das Phänomen erweist sich in vielen Fällen klassischen Streuexperimenten mit elektromagnetischer Strahlung überlegen, weil bei letzterer die relativen Energieänderungen nur gering sind, was insbesondere Untersuchungen von Bewegungsvorgängen beschränkt. Aber auch bei den rein