# Magnetic small-angle scattering from Cu-17 at.% Mn

# Magnetic small-angle scattering from Cu-17 at.% Mn

B Schönfeld†, O Paris†§, G Kostorz† and J Skov Pedersen‡

† Institut für Angewandte Physik, Eidgenössische Technische Hochschule Zürich, CH-8093 Zürich, Switzerland
‡ Department of Solid State Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark

**Abstract.** Two Cu-17 at.% Mn single crystals quenched to room temperature after aging at 483 and 553 K, respectively, were investigated by small-angle neutron scattering between room temperature and 15 K. While nuclear small-angle scattering is low and increases only slightly towards the direct beam, strong magnetic small-angle scattering is observed. Its intensity increases with increasing degree of chemical short-range order and decreasing temperature. The correlation lengths for chemical and (static) ferromagnetic fluctuations are comparable.

## 1. Introduction

Cu-rich Cu–Mn alloys in the $\gamma$ solid solution range exhibit two features that have attracted repeated interest: the possibility of the occurrence of intermetallic phases and spin-glass behaviour. Although not supported by experimental microstructural evidence, intermetallic phases around the stoichiometry of $Cu_3Mn$ and $Cu_5Mn$ are given in the recent phase diagram compilation by Massalski [1]. The results of differential thermal analysis together with hardness measurements and electrical resistivity data (which led to the suggestion of the existence of intermetallic phases) by Sokolovskaya *et al* [2] were confirmed by Köster and Gödecke [3]. Furthermore, high-temperature and room-temperature modifications of $Cu_5Mn$ were suggested by Gödecke [4] based on measurements of thermal expansion and electrical resistivity.

Chemical and magnetic short-range order of the $\gamma$ solid solution has repeatedly been investigated by diffuse wide-angle neutron scattering from single crystals [5–9]. While chemical short-range order scattering exhibits diffuse maxima at $1\frac{1}{2}0$ positions, magnetic short-range order scattering shows peaks at $000$ and $1\frac{1}{2}\pm\delta\,0$ positions, with $\delta$ depending on the composition of the alloy.

Chemical short-range order was characterized in terms of Warren–Cowley short-range order parameters by Wells and Smith for Cu with 15 and 25 at.% Mn [5], for Cu-25 at.% Mn by Hirabayashi *et al* [6] and Cable *et al* [7], and for Cu-17 at.% Mn by Roelofs *et al* [8]. Only in [8] was a well-defined thermodynamic state investigated. In measurements taken at room temperature, the magnetic scattering (often treated in the quasi-elastic approximation) can be identified via the rapid decrease of the magnetic form factor with the scattering vector [5, 6] or by neutron-polarization analysis [7]. From their data, Roelofs *et al* [8] concluded that at room temperature magnetic scattering is negligible. This is similar to the conclusion reached by Cable *et al* [7] that spins become completely uncorrelated above about 350 K.

§ Present address: Institut für Metallphysik, Montanuniversität, A-8700 Leoben, Austria.

Cable *et al* [7] introduced various spin-correlation models to discuss the magnetic scattering around $1\frac{1}{2}0$ positions. Magnetic wide-angle scattering far below the spin-glass temperature was measured by Roelofs *et al* [10] for Cu-17 at.% Mn and by Murani *et al* [9] for Cu-5 at.% Mn. The elastic–inelastic nature of magnetic scattering around $1\frac{1}{2}0$ was studied by Werner *et al* [11] and for selected positions also by Murani and Tholence [12]. Above the spin-glass temperature, magnetic scattering becomes progressively inelastic [11].

Gray *et al* [13] reported on small-angle neutron scattering (SANS) of Cu-16.7 at.% Mn as a function of temperature (5 to 220 K). They represented the spin correlations in terms of a radius of gyration. As they used no well-defined thermodynamic state for atomic short-range order, and also took data at 220 K as representing pure nuclear scattering, a more extensive investigation of magnetic small-angle scattering as a function of the degree of order and of temperature is presented in the following. By controlling the degree of order, it is also possible to check the suggestion of Ling *et al* [14] that, according to electronic-structure calculations, scattering around $0\,0\,0$ is expected to decrease when lowering the degree of short-range order.

## 2. Experimental details

From **Cu**Mn single crystals grown by the Bridgman technique, two cylindrically shaped samples ($\sim$ 10 mm in height and diameter, cylinder axis close to $\langle 111 \rangle$) were cut by spark erosion. The manganese concentration determined by x-ray fluorescence and chemical analysis was 17.2(2) at.% for sample 1 and 16.6(2) at.% for sample 2. The samples were homogenized at 1123 K and water quenched. Sample 1 was then aged at 483 K for 2 weeks, sample 2 at 553 K for 2 days, and both were water quenched. The aging conditions were chosen to set up well-defined states of thermal equilibrium [15]. Sample 1 had been previously used to determine atomic short-range order by diffuse wide-angle scattering [8].

Small-angle scattering experiments were performed at the SANS instrument at Risø National Laboratory, Denmark. Neutrons with an average wavelength $\lambda = 6$ Å ($\delta\lambda/\lambda \approx$ 0.18 full width at half maximum) were used to record the SANS signal with a two-dimensional position-sensitive detector at a distance of 1 m from the sample. This corresponds to scattering vectors $q$ ($q = 4\pi \sin\theta/\lambda$, $2\theta =$ scattering angle) ranging from 0.03 to 0.23 Å$^{-1}$. Data were taken between room temperature and 15 K using a Displex cryostat. The SANS data did not show any azimuthal dependence, and the scattering was azimuthally averaged to improve counting statistics. As the typical signal-to-background ratio was only about 3:1, the data were corrected for background after averaging. They were converted to scattering cross-sections using the elastic incoherent scattering from water. A comparative calibration with single-crystalline vanadium agreed within $\pm$ 5%. No attempts were made to correct for instrumental resolution, as the curves varied only slowly with the modulus of the scattering vector.

## 3. Results and discussion

The total macroscopic differential scattering cross-section $d\Sigma/d\Omega$ (the microscopic differential scattering cross-section multiplied by the atomic density) is given in figure 1 for both samples at room temperature and at 15 K. The contribution from elastic incoherent scattering, atomic short-range order scattering (approximated by setting it to 1 Laue unit; 1 Laue unit corresponds to the diffuse scattering of a random solid solution), and paramagnetic scattering is indicated by the dotted line.
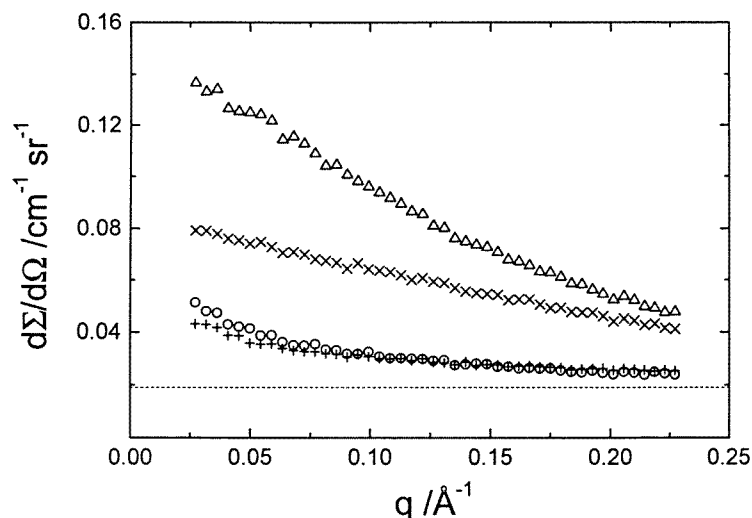
**Figure 1.** Small-angle neutron scattering of Cu-17 at.% Mn after aging at 483 K (sample 1: ∘, △) and 553 K (sample 2: +, ×); first symbol: data taken at room temperature, second symbol: data taken at 15 K. The sum of elastic incoherent scattering, monotonic Laue scattering, and paramagnetic scattering is indicated by the dotted line.

At room temperature the scattering curves nearly coincide. A slight increase towards the direct beam is observed. This could originate from chemical (nuclear) and/or magnetic contributions. Assuming chemical correlations, a typical correlation length can be estimated by fitting the curves to a Lorentzian-squared function

$$\frac{d\Sigma}{d\Omega}(q) = \frac{B}{(1 + q^2\xi_2^2/6)^2} \tag{1}$$

where $B$ is the cross-section at $q = 0$ and $\xi_2$ the correlation length. The fitting parameters are given in table 1. The length scale $\xi_2$ of sample 1 is comparable to the range for which Warren–Cowley short-range order parameters are sufficiently different from zero for this sample [8]. Following Gray *et al* [13], equation (1) was also replaced by a Lorentzian function or by the so-called Debye function, which describes the scattering of monodisperse Gaussian coils [16]. The correlation lengths found for all three functions are very similar. The reason for choosing the Lorentzian-squared function will be given below, following equation (2).

Whether chemical inhomogeneities on the length scale of these correlation lengths are precursors of any two-phase regime remains speculative. Certainly a second phase is not expected on the basis of the phase diagram, even when considering the two-phase ranges

**Table 1.** Fitting parameters to equation (1) for the nuclear scattering at room temperature using a fixed background of 0.019 cm$^{-1}$ sr$^{-1}$. Only data for positions with $q > 0.05$ Å$^{-1}$ were used.

|  | Aging temperature (K) | $B$ (cm$^{-1}$ sr$^{-1}$) | $\xi_2$ (Å) |
|---|---|---|---|
| Sample 1 | 483 | 0.019(1) | 11.4(3) |
| Sample 2 | 553 | 0.015(1) | 8.6(3) |

involving the suggested intermetallic phases. A weak increase in nuclear scattering was also observed for polycrystalline Cu-16.7 at.% Mn at room temperature [17]. Even though single crystals were used in the present investigation, it may be argued that there are always scattering contributions from surface layers and dislocations (see, e.g., [18]). However, it seems safe to exclude these possibilities; surfaces because of the sample thickness of 10 mm, which gives a large preponderance of volume scattering, and dislocations because of the relatively high scattering vectors (see, e.g., [19]).
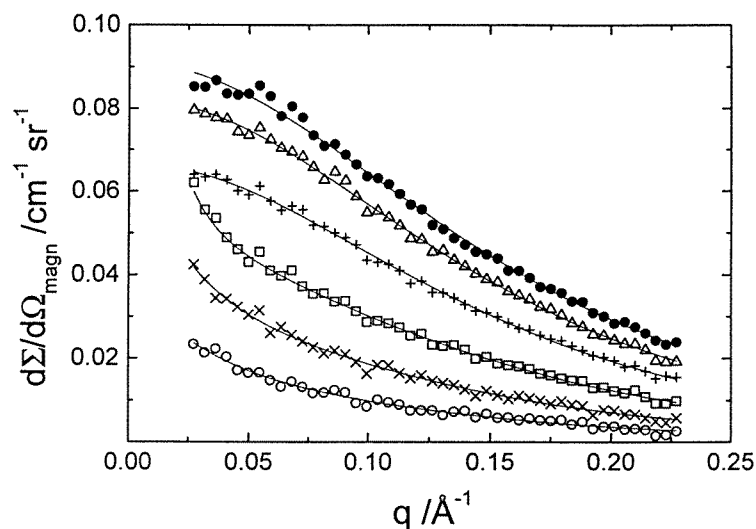


**Figure 2.** Magnetic small-angle neutron scattering of Cu-17.2 at.% Mn (sample 1), at 200 K (○), 160 K (×), 120 K (□), 80 K (+), 40 K (△), and 15 K (●). The solid lines are best fits to the data using equation (2).

At 15 K the scattering curves of both samples are distinctly different; as conjectured by Ling *et al* [14], the magnetic scattering decreases as the degree of short-range order decreases. This effect is quite drastic, as the degree of short-range order of the two samples was not much changed according to the room temperature data. Magnetic scattering was investigated in detail for sample 1, which shows the larger effect. It was obtained by subtracting the room-temperature curve from the total scattering. The scattering cross-section is found to increase continuously with decreasing magnitude of the scattering vector, indicating ferromagnetic spin correlations (figure 2). It is obvious that there is a striking difference in the shape of the curves at small $q$ values above and below 80 K, i.e., near the spin-glass temperature ($\sim$75 K for Cu-16.7 at.% Mn [20]); while the scattering cross-section continuously increases with decreasing temperature at high $q$ values, there is a cusp at about 80 K at the lowest $q$ values. Such a maximum is commonly found at the spin-glass temperature [12].

Magnetic small-angle scattering data from spin glasses are often described by exponentially damped ferromagnetic spin correlations which lead to a Lorentzian shape of the scattering curves. However, such a model fails to describe the data presented in figure 2 for all temperatures. Therefore the sum of a Lorentzian and a Lorentzian-squared function was used

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(q) = \frac{A}{1 + q^2\xi_1^2/3} + \frac{B}{(1 + q^2\xi_2^2/6)^2} \tag{2}$$

where $\xi_1$, $\xi_2$ are the correlation lengths and $A$, $B$ the corresponding cross-sections at $q = 0$. Equation (2) is constructed in such a way that the expansion for low $q$ values follows the well-known Guinier approximation of small-angle scattering for both terms independently, which means that $\xi_1$ and $\xi_2$ may also be interpreted as radii of gyration. Such model scattering cross-sections were also used in other magnetic small-angle scattering investigations of spin glasses (see, e.g., [13, 21]) to reproduce a $q^{-2}$ and $q^{-4}$ intensity variation at large and small $q$ values, respectively. The Lorentzian and the Lorentzian-squared terms correspond to spin correlations varying as $\exp(-r/\xi_1)/r$ and $\exp(-r/\xi_2)$, respectively.

**Table 2.** Fitting parameters to equation (2) for the magnetic scattering from samples 1 and 2.

| | $T$ (K) | $A$ (cm$^{-1}$ sr$^{-1}$) | $\xi_1$ (Å) | $B$ (cm$^{-1}$ sr$^{-1}$) | $\xi_2$ (Å) |
|---|---|---|---|---|---|
| Sample 1 | 200 | 0.018(3) | 46(15) | 0.012(3) | 12.0(9) |
| | 160 | 0.036(6) | 68(16) | 0.026(3) | 12.2(5) |
| | 120 | 0.150(100) | > 100 | 0.043(2) | 11.5(3) |
| | 80 | 0 | — | 0.067(1) | 11.3(1) |
| | 40 | 0 | — | 0.083(1) | 11.1(1) |
| | 15 | 0 | — | 0.091(1) | 10.7(1) |
| Sample 2 | 80 | 0 | — | 0.028(1) | 8.4(2) |
| | 15 | 0 | — | 0.040(1) | 7.8(2) |

The solid lines in figure 2 show the best fits, and the corresponding parameters are summarized in table 2. While both terms are needed to fit the data above 80 K, only the Lorentzian-squared term (it may again be replaced by a Debye function, but not by a Lorentzian function) is required below 80 K.

The correlation lengths $\xi_1$ and $\xi_2$ show a different temperature dependence; while $\xi_1$ increases when approaching the spin-glass temperature from above, $\xi_2$ varies smoothly across the spin-glass temperature and shows nearly no temperature dependence. Therefore, the following interpretation is suggested. While the Lorentzian term represents dynamic ferromagnetic spin correlations for which the correlation length increases when approaching the spin-glass temperature from above, the Lorentzian-squared term stems from the static correlations. This separation in elastic and inelastic contributions is supported by the results of Murani and Tholence [12] and Werner *et al* [11] who used various spectrometer resolutions in neutron-scattering experiments.

The correlation length $\xi_2$ for sample 2, the sample with the lower degree of short-range order, is smaller. This may be compared with the correlation between chemical and magnetic short-range order. Cable *et al* [7] noted that the magnetic peak at $1\frac{1}{2}0$ (due to correlations within the ferromagnetic 'clusters') and the nuclear peak (due to chemical short-range order) at the same position have approximately the same width, i.e., yield the same correlation length. Atomic and magnetic short-range order parameters also closely agree in sign (for the first 15 shells) and scaled magnitude as noted from the earlier diffuse wide-angle scattering experiments [8, 10]. This means that starting from a Mn atom as central atom, positive values of the Warren–Cowley short-range order parameters (preference for Mn neighbours) are connected with positive values of the magnetic short-range order parameters and thus a ferromagnetic correlation.

## 4. Conclusions

In the present evaluation it was shown that the correlation lengths for chemical concentration fluctuations and static ferromagnetic spin correlations coincide for both samples. This correspondence was demonstrated by comparing two alloys of similar compositions but with different well-defined states of chemical short-range order.

The slight increase in scattering towards the direct beam at room temperature is tentatively attributed to first indications of the $\alpha-\gamma$ two-phase regime. A proof that no other phase or magnetic scattering is involved may be obtained from x-ray scattering. Because of the small difference in the number of electrons of Cu and Mn, synchrotron radiation is required as the scattering contrast must be enhanced, e.g., by choosing a wavelength near the Mn K absorption edge (anomalous dispersion). First results from wide-angle scattering using synchrotron radiation [22] give no compelling reason to attribute part of the room-temperature scattering to magnetic scattering.

## References

[1]   Massalski T B 1990 *Binary Alloy Phase Diagrams* 2nd edn, vol 2 (Materials Park, OH: ASM International)
[2]   Sokolovskaya E M, Grigor'ev A T and Smirnova E M 1962 *Russ. J. Inorg. Chem.* **7** 1370
[3]   Köster W and Gödecke T 1989 *Z. Metallkde.* **80** 761
[4]   Gödecke T 1990 *Z. Metallkde.* **81** 826
[5]   Wells P and Smith J H 1971 *J. Phys. F: Met. Phys.* **1** 763
[6]   Hirabayashi M, Koiwa M, Yamaguchi S and Kamata K 1978 *J. Phys. Soc. Japan* **45** 1591
[7]   Cable J W, Werner S A, Felcher G P and Wakabayashi N 1984 *Phys. Rev.* B **29** 1268
[8]   Roelofs H, Schönfeld B, Kostorz G and Bührer W 1995 *Phys. Status Solidi* b **187** 31
[9]   Murani A P, Schärpf O, Andersen K and Raphel R 1996 *Institute Laue–Langevin Annual Report* p 62
[10]  Roelofs H, Schönfeld B, Kostorz G, Bührer W, Robertson J L, Zschack P and Ice G E 1996 *Scripta Mater.* **34** 1393
[11]  Werner S A, Rhyne J J and Gotaas J A 1985 *Solid State Commun.* **56** 457
[12]  Murani A P and Tholence J L 1977 *Solid State Commun.* **22** 25
[13]  Gray E M, Hicks T J and Smith J H 1982 *J. Phys. F: Met. Phys.* **12** L189
[14]  Ling M F, Staunton J B and Johnson D D 1994 *J. Phys.: Condens. Matter* **6** 6001
[15]  Reihsner R and Pfeiler W 1985 *J. Phys. Chem. Solids* **46** 1431
[16]  Kirste R G and Oberthür R C 1982 Synthetic polymers in solution *Small-Angle X-ray Scattering* ed O Glatter and O Kratky (London: Academic) p 387
[17]  Gray E M and Smith J H 1975 *J. Phys. F: Met. Phys.* **5** L171
[18]  Kostorz G 1996 X-Ray and Neutron Scattering *Physical Metallurgy* ed R W Cahn and P Haasen (Amsterdam: North-Holland) p 1115
[19]  Lepistö T K, Kostorz G, Kuokkala V T and Kettunen P 1991 *Mater. Sci. Eng.* A **131** 171
[20]  Gray E M 1996 *J. Phys.: Condens. Matter* **8** 751
[21]  Greedan J E, Raju N P, Maignan A, Simon Ch, Pedersen J S, Niraimathi A M, Gmelin E and Subramanian M A 1996 *Phys. Rev.* B **54** 7189
[22]  Roelofs H 1995 Paarkorrelationen im Spinglas Cu-17 at.% Mn *Dissertation No 11008* ETH Zürich