Analytical behavior of short-range order scattering of Cu-rich Cu-Mn near the Γ point

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Small-angle neutron scattering with scattering vectors in the range of 0.01 to 0.17 reciprocal lattice units was measured for a single crystal of Cu-17.2 at.% Mn aged at 483 K. At large scattering vectors, a directional dependence of the scattering intensity is observed, with slightly higher values along $\langle 100 \rangle$ than along $\langle 110 \rangle$. The difference in intensities continuously decreases with decreasing scattering vector. The present data contradict the results of a previous synchrotron radiation study where it was concluded that short-range order scattering is nonanalytical at the Γ point. The discrepancy is traced back to multiple Bragg scattering with high-energy x rays.

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I. INTRODUCTION

Small-angle scattering with x rays and neutrons is frequently employed to characterize scattering inhomogeneities on a length scale of 1 to several 100 nm (for a review, see, e.g., Kostorz¹). Solid solutions were occasionally investigated with this technique in context with wide-angle scattering experiments to get the correct scattering pattern close to 000 (Γ point). This range of reciprocal space is required for the determination of short-range order scattering, especially for alloys with large atomic displacements (see, e.g., Schönfeld²). Neglecting this range may lead to erroneous conclusions [see, e.g., the discussion on the shape of Guinier-Preston I zones in Al-rich Al-Cu (Ref. 3 and references therein)].

While the scattering intensity might approach the origin of reciprocal space with different slopes as a function of the scattering vector for anisotropic scattering objects, no difference on the absolute intensity (when extrapolated towards 000) has ever been reported. Also, solid solutions were never observed to show different values of the scattering intensity at 000 upon extrapolation from different directions in reciprocal space.

Recently, Reichert and co-workers⁴ reported a nonanalytical behavior in short-range order scattering at 000. This conclusion was reached on the basis of a synchrotron radiation study of Cu-17 at.% Mn and a separation of the effective pair interaction parameters into a chemical and a strain-induced part (see also Bugaev and co-workers⁵). Nonanalytical behavior in short-range order scattering at 000 was associated with a nonanalytical behavior of the Fourier transform of these effective pair interaction parameters. With such a parametrization the diffuse scattering for two azimuthal scans (with scattering vectors of 0.45 and 1.1 reciprocal lattice units, Fig. 5 in Ref. 4) could be reproduced. The attempt to judge the behavior at 000 from intensities with such large scattering vectors was criticized by Chepulskii and Tatarenko⁶ (see also the Reply by Reichert and co-workers⁷).

Cu-rich Cu-Mn has been repeatedly investigated (see Roelofs and co-workers⁸ and references therein). Such a nonanalytical behavior had never been noted in any wide-

angle scattering experiment. As small-angle neutron scattering (SANS) from a slice of single-crystalline Cu-17 at.% Mn with a $\langle 100 \rangle$ surface normal can easily clarify the intensity pattern in the scattering vector range of the experiments of Refs. 4 and 7, such an experiment has now been performed.

II. EXPERIMENT

A Cu-Mn single crystal was grown by the Bridgman technique. A cylindrically shaped sample (about 10 mm in height and diameter) was cut, homogenized at 1123 K, aged at 483 K for 2 weeks and rapidly quenched to room temperature. Its composition as determined by x-ray fluorescence and chemical analysis was Cu-17.2(2) at.% Mn. Previously, this sample had been used in a wide-angle diffuse scattering experiment of Roelofs and co-workers⁸ and in a small-angle neutron scattering experiment of Schönfeld and co-workers.⁹ From this cylindrically shaped sample, a slice with a $\langle 100 \rangle$ surface normal, 3 mm in thickness and about 9 mm in diameter, was cut by spark erosion.

The experiment was performed at the small-angle neutron scattering facility SANS-I (PSI, Villigen, Switzerland). Neutrons of a wavelength of 0.66 nm [$\Delta\lambda/\lambda = 10\%$ full width at half maximum (FWHM)] were registered with a two-dimensional ³He detector at sample-detector distances of 2 and 4 m using a collimation of 4.5 m. Scattering vectors within 0.01 and 0.17 reciprocal lattice units (r.l.u.) were accessible. To convert the scattering intensities into absolute scattering cross sections, background with an empty sample holder and a boron nitride sample blocking the direct beam were measured, and the scattering of single-crystalline vanadium was used for calibration. Coherent scattering lengths, elastic incoherent scattering cross sections, and absorption cross sections were taken from Sears.¹⁰ For Cu-Mn and V, the calculated and measured transmissions agreed within 3%.

III. SMALL-ANGLE NEUTRON SCATTERING

The total macroscopic differential scattering cross section (in Laue units, 1 L.u., corresponding to the short-range order scattering of a random solid solution) after subtracting the

FIG. 1. Small-angle neutron scattering in Laue units from Cu-17.2 at.% Mn for the (001) plane.

incoherent scattering is shown in Fig. 1. At large scattering vectors, scattering intensities are higher along $\langle 100 \rangle$ than along $\langle 110 \rangle$. For a detailed comparison, sector averages (within $\pm 15^\circ$) around the two directions were performed (Fig. 2). The intensities along both directions steadily approach each other with decreasing scattering vector. At the smallest scattering vectors, the error bars based on counting statistics (typically 1% for 2 m and 5% for 4 m sample-detector distance), overlap.

The present result is corroborated by the previous SANS investigation of Schönfeld and co-workers⁹ where no azimuthal dependence was observed for a crystal orientation of lower symmetry (neutrons were incident along the cylinder axis that was about 10° off $\langle 111 \rangle$). The scattering intensities of the former study (Fig. 1 in Ref. 9) and the azimuthally averaged data of the present investigation closely agree.

IV. WIDE-ANGLE SCATTERING

In Fig. 3, wide-angle neutron scattering intensities based on the investigations of Roelofs and co-workers⁸ are shown.

FIG. 2. Calibrated small-angle scattering in Laue units from Cu-17.2 at.% Mn along $\langle 100 \rangle$ (filled circles) and $\langle 110 \rangle$ directions (open circles) are shown for the sample-detector distances of 2 and 4 m (inset). Typical error bars for the 2 m setup are of the size of the symbols, and for the 4 m setup 3 times the symbol size.

FIG. 3. Recalculated short-range order scattering in Laue units based on the data of Roelofs and co-workers (Ref. 8, filled circles) and as determined in the present work where small-angle neutron scattering has also been considered (open triangles).

In their investigation, scattering vectors ranged from 0.15 to 2.67 r.l.u. Using the fitted Warren-Cowley short-range order parameters (Table I in Ref. 8) to extrapolate short-range order scattering towards 000, two features are noted; (i) a general increase towards 000 and (ii) slightly higher intensities along $\langle 100 \rangle$ than along $\langle 110 \rangle$. The absolute values, however, indicate that measurements at small scattering vectors are required to give the correct magnitude.

Combining the present SANS data and the original wide-angle scattering intensities in a least-squares fitting procedure with an unchanged number of fitting parameters (41 Warren-Cowley short-range order parameters α_{lmn}^x and 40 linear displacement parameters γ_{lmn}^x , lmn being the shell index in units of half the lattice parameter), the short-range order parameters differ by 4 standard deviations while the linear displacement parameters remain within 2 standard deviations. The recalculated short-range order scattering close to the direct beam along $\langle 100 \rangle$ and $\langle 110 \rangle$ now increases much stronger (Fig. 3).

Higher scattering intensities along $\langle 100 \rangle$ than along $\langle 110 \rangle$ are also seen in the as-measured scattering pattern of Reichert and co-workers⁴ for scattering vectors larger than ~ 0.3 r.l.u. However, the two scans shown in Ref. 7 for 0.15 r.l.u. and larger values are incompatible with the present results, as intensities in $\langle 100 \rangle$ and $\langle 110 \rangle$ differ by more than a factor of 2 and not by less than $\sim 15\%$ as in the present work. Unfortunately, a comparison of the individual scans on an absolute scale is impossible as the x-ray data are uncalibrated.

While multiple Bragg scattering was avoided in the present investigation by the choice of a sufficiently large wavelength, it must have affected the data in the synchrotron radiation study, where x-rays with wavelengths of 0.012 to 0.018 nm were employed. Sample mosaicity of about 0.2° (this is the typical value of Cu-Mn single crystals grown in the authors' laboratory from which the sample of Ref. 4 also originates) will barely lead to multiple scattering unless long tails in scattering are invoked. Contamination by harmonics (mentioned in Ref. 4) and an energy resolution $\Delta E/E$ of about 10^{-3} (Ref. 11) (i.e., larger than 0.017 r.l.u.), however, lead to an overlap of the smeared Ewald sphere and the 200 Bragg reflection of the $\lambda/2$ harmonics. This interpretation is further supported by the shape of the scans in Ref. 7. Close

resemblance is seen with the present wide-angle neutron scattering data along $\langle 110 \rangle$, but large differences occur along $\langle 100 \rangle$.

In summary it is concluded that there is no experimental proof of a nonanalytical behavior of the scattering function of Cu–17.2 at.% Mn.

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