Structure of Cd-Ga Melts Part 2: X-Ray Small-Angle Scattering

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X-ray small-angle scattering experiments were performed on nine melts of the Cd-Ga system at different temperatures up to 440°C. Evaluation of the data follows the Ornstein-Zernike theory of critical scattering, thus yielding correlation lengths ξ of concentration fluctuations and the long-wavelength limit $S_{\rm CC}$ (0) of the Bhatia-Thornton structure factor. Studies of the concentration and temperature dependence of ξ and $S_{\rm CC}$ (0) indicate that the critical point occurs at $c_{\rm C}=50.0\pm1.0$ at % Ga and $T_{\rm C}=295.2\pm0.1^{\circ}$ C. For a melt with the critical concentration, $S_{\rm CC}$ (0) increases up to 3500 times the ideal $S_{\rm CC}^{\rm cd}$ (0)= $c_{\rm A}c_{\rm B}$. This indicates a strong segregation tendency. In the vicinity of the critical point of the Cd-Ga system, experimental correlation lengths $\xi > 100$ Å were obtained. The critical-point exponents ν and γ were determined. It follows that the behaviour of a critical Cd-Ga melt satisfies the prediction of the classical mean-field theory for higher temperatures, whereas, within experimental accuracy, the lattice-gas predictions are satisfied upon approaching the critical temperature.

1. Introduction

In binary melts with segregation tendency, the concentration fluctuations produce an increase of the scattered intensity at small momentum transfers. The analysis of this so-called small-angle scattering yields informations concerning the range of correlated concentration fluctuations.

The most interesting effects can be expected for systems exhibiting a miscibility gap in the liquid state. In the vicinity of the critical point of the miscibility gap, long-range concentration fluctuations may appear in the homogeneous phase giving rise to critical small-angle scattering.

Until now, small-angle scattering has only been observed in melts of the following binary metallic systems: Ag-Ge [1], Au-Cs [2], Bi-Cu [3], Bi-Ga [4], Bi-Zn [4], Ga-Pb [4], and Li-Na [5] by neutron scattering and Al-In [6], Al-Sn[7], Cs-Na [8], and Li-Na [9] by X-ray scattering.

In the present work the Cd-Ga system was investigated by means of small-angle X-ray scattering (SAXS).

The SAXS-experiments performed on binary metallic melts up to now may be divided, essentially, into two classes:

1. investigations concerning the concentration dependence of the small-angle scattering without

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- observation of the temperature dependence; by means of those experiments, short-range concentration fluctuations of about one coordination sphere were detected [6, 7, 8];
- 2. investigations with regard to the temperature dependence of the critical scattering. Only *one* melt has been considered with a critical concentration [9].

In the present work, temperature dependent X-ray small-angle scattering was performed for the first time on a large concentration range of the homogeneous liquid phase of a binary metallic system with a miscibility gap. This investigation yielded information about the range of concentration fluctuations and various thermodynamic quantities, and enabled the critical-point exponents, ν and ν , to be calculated.

2. Theoretical Fundamentals

2.1. Partial structure factors (q=0) and thermodynamics

The total structure factor S(q) calculated from the coherently scattered intensity $I_{coh}(q)$ can be separated into three partial structure factors according to Bhatia and Thornton [10]:

$$S(q) = \frac{I_{\text{coh}}(q)}{\langle f^2 \rangle} = \frac{\langle f \rangle^2}{\langle f^2 \rangle} S_{\text{NN}}(q) + \frac{(\Delta f)^2}{\langle f^2 \rangle} S_{\text{CC}}(q) + \frac{2\langle f \rangle \Delta f}{\langle f^2 \rangle} S_{\text{NC}}(q)$$

$$(1)$$

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where f = the scattering amplitude, $\Delta f = f_{\rm A} - f_{\rm B}$, $\langle f \rangle = c_{\rm A} f_{\rm A} + c_{\rm B} f_{\rm B} (c_{\rm i} = {\rm atomic} \ {\rm fraction} \ {\rm of} \ {\rm component} \ {\rm i})$. $S_{\rm NN}(q)$ and $S_{\rm CC}(q)$ are the Fourier transforms of the local atomic density and concentration fluctuations, respectively, and $S_{\rm NC}(q)$ is the crossterm.

 $S_{NN}(q)$ describes the contribution of the overall structure to the total structure factor and $S_{CC}(q)$ the contribution of the chemical short-range order. $S_{CC}(q)$ has the following features:

- 1. $S_{CC}(q) = c_A c_B$ for a random distribution of the atoms or an ideal solution, respectively;
- 2. if unlike neighbouring-atoms are preferred in the melt, i.e., compound formation, $S_{\rm CC}(q)$ exhibits a distinct peak at lower q-values than the main peak of $S_{\rm NN}(q)$ and some damped oscillations. $S_{\rm CC}(0)$ is then smaller than $c_{\rm A}c_{\rm B}$; and
- 3. if like neighbouring-atoms are preferred in the melt, i.e., segregation tendency, $S_{\rm CC}(q)$ increases for low q-values giving rise to small-angle scattering in a scattering experiment. For higher q-values $S_{\rm CC}(q)$ shows some damped oscillations.

In the long-wavelength limit, q=0, the Bhatia-Thornton structure factors may be expressed directly in terms of various thermodynamic quantities. $S_{NN}(0)$ and $S_{CC}(0)$ represent the mean-square fluctuation of the number density and of the concentration in a subsystem and $S_{NC}(0)$ denotes the coupling of these fluctuations. From statistical thermodynamics it follows that

$$S_{\rm CC}(0) = N \langle (\Delta c)^2 \rangle = N k_{\rm B} T / \left(\frac{\partial^2 G}{\partial c_{\rm A}^2} \right)_{p, T, N},$$
 (2)

$$S_{\rm NC}(0) = \langle \Delta N \Delta c \rangle = -\vartheta S_{\rm CC}(0),$$
 (3)

$$\begin{split} S_{\text{NN}}(0) &= \frac{\langle (\Delta N)^2 \rangle}{N} \\ &= \varrho_0 k_{\text{B}} T \varkappa_T + \vartheta^2 S_{\text{CC}}(0) \,, \end{split} \tag{4}$$

where N = number of atoms, $k_B =$ Boltzmann constant, T = temperature [K], $\varkappa_T =$ isothermal compressibility, G = Gibbs free energy,

$$\vartheta = \frac{1}{V_{\text{M}}} \left(\frac{\partial V_{\text{M}}}{\partial c_{\text{A}}} \right) = \text{dilatation factor},$$

 $V_{\rm M} = {\rm molar \ volume.}$

In Eqns. (2) to (4) $\langle \rangle$ indicates the thermal average. Since $S_{NC}(0)$ can directly be expressed in terms of $S_{CC}(0)$, in the long-wavelength limit, q=0, the

coherent intensity may be written as the sum of two terms only.

Using Eqn. (1), the following expression exists for the coherent intensity at q=0:

$$I_{\text{coh}}(0) = \varrho_0 k_{\text{B}} T \varkappa_T \langle f \rangle^2 + S_{\text{CC}}(0)$$

$$\cdot [\vartheta \langle f \rangle - \Delta f]^2$$

$$= A \varkappa_T + B S_{\text{CC}}(0).$$
(5)

The concentration fluctuations and thus $S_{\rm CC}(0)$ only contribute to the scattered intensity $I_{\rm coh}(0)$, if the coefficient B does not vanish. To give an estimation of the value of B, the dilatation factor, ϑ , may in the case of Cd-Ga melts, be expressed as $\vartheta = \varrho_0(v_{\rm A} - v_{\rm B})$, where $v_{\rm A}$ and $v_{\rm B}$ are the atomic volumes of the pure components A and B, respectively. Thus one obtains

$$B = [\rho_0 v_{\rm A} v_{\rm B}]^2 \ (\rho_{\rm A}^{\rm el} - \rho_{\rm B}^{\rm el})^2, \tag{6}$$

where $\varrho_i^{el} = f_i/v_i$, the electronic density of the species i. Thus, in the case of X-ray scattering, the difference in the electronic density of the constituents makes the concentration fluctuations visible. It is noted, that the difference in electronic density between a colloidal particle and its solvent is used to describe qualitatively and quantitatively the small-angle scattering of colloidal solutions.

Principally, the intensity scattered by the number density fluctuations and by the concentration fluctuations cannot be determined independently in one scattering experiment. A calculation of $S_{\rm CC}(0)$ from the scattered intensity extrapolated to q=0 thus requires knowledge of the compressibility, \varkappa_T , which can be calculated from, for example, ultrasonic velocity measurements.

Additionally, data should be available about the partial molar volumes of the components in the liquid alloy, extracted from density measurements.

The transition from the one-melt to the two-melt region at the critical point, defined by the critical concentration, $c_{\rm c}$, and the critical temperature, $T_{\rm c}$, is a second order phase transition. This transition is characterized by long-range fluctuations of the order parameter. The appearence of long-range concentration fluctuations upon approaching the critical point causes the divergence of $S_{\rm CC}(0)$ according to Equation (2). Following Stauffer [11], the change of the compressibility at the critical point is negligible compared to $S_{\rm CC}(0)$. It shows normal behaviour and is not influenced by the diverging range of the concentration fluctuations. According to Eqn. (5), the cohe-

rent intensity is, in the vicinity of the critical point, thus determined by the second term containing $S_{\rm CC}(0)$. The first term, containing \varkappa_T , only yields a small contribution to the scattering signal, being only slightly dependent on the temperature and nearly independent of q for small momentum transfers.

2.2. Critical scattering

The classical theory of critical scattering by one-component fluids at the liquid-gas-transition has been developed by Ornstein and Zernike [12]. Upon applying the Ornstein-Zernike theory to the interpretation of the small-angle scattering caused by concentration fluctuations in binary melts, the Bhatia-Thornton structure factor $S_{\rm CC}(q)$ can, for small momentum transfers q, be described by a Lorentzian:

$$S_{\rm CC}(q) = S_{\rm CC}(0)/(1 + \xi^2 q^2)$$
. (7)

The appropriate graph for such a scattering curve is a plot of $S_{\rm CC}(q)^{-1}$ versus q^2 , the so-called Ornstein-Zernike plot (OZ plot). If the scattering curve has the shape of a Lorentzian, the Ornstein-Zernike plot yields a straight line. From the slope and intercept of this line, $S_{\rm CC}(0)$ and the correlation length, ξ , can be calculated. A scattering curve, according to Eqn. (7), presumes a correlation function of the form

$$G(r) = A \exp\left\{-\frac{r}{\xi}\right\}/r. \tag{8}$$

The parameter ξ , called the **co**rrelation length, describes the spatial range of correlated fluctuations.

2.3. Critical-point exponents

The temperature dependence of ξ and $S_{\rm CC}(0)$ can be expressed in the form of a power law for small values of the reduced temperature, $\varepsilon \equiv (T-T_{\rm c})/T_{\rm c}$:

$$\xi = \xi_0 \, \varepsilon^{-\nu} \,, \tag{9}$$

$$S_{\rm CC}(0) = K T \varepsilon^{-\gamma}. \tag{10}$$

K is a constant and ν and γ are the so-called critical exponents. In addition, the following scaling relation holds:

$$\nu(2-\eta) = \gamma. \tag{11}$$

The critical exponent, η , describes deviations from the Ornstein-Zernike theory which are to be expected very close to the critical point according to Fisher [13].

There are essentially two models for the critical behaviour of binary liquids, namely the classical mean-field theory and the lattice-gas model, which yield different values for the critical exponents ν , γ , and η :

mean-field theory:

$$\gamma = 0.5$$
, $\gamma = 1.0$, $\eta = 0$,

lattice-gas model:

$$\nu = 0.63$$
, $\gamma = 1.24$, $\eta = 0.032$.

In the case of binary metallic melts with limited solubility only a few experimental determinations of the critical exponents are known. The main reason might be that for the investigation of metallic liquids only the method of neutron or X-ray scattering at small momentum transfers can be used and that no light scattering experiments are possible.

3. Experiments

Concerning the characteristics of the Cd-Ga system, the experimental apparatus, the sample preparation and containers, and the performance of experiments, see [14]. As window material for the containers, mica was used, as the materials normally used in the high-angle experiments, such as sintered Be [15] or amorphous graphite [16], show strong and temperature dependent small-angle scattering, which is very difficult to correct for. With regard to the temperature stability and gradients in the sample we refer to [14].

The collimation in the small-angle scattering apparatus used was achieved by a Kratky-type collimation system with a rectangular beam profile. Thus, a collimation correction or "desmearing" procedure had to be performed, which was done according to [17] with smoothed experimental curves [18].

4. Results and Discussion

4.1. Intensity curves

Figure 1 shows the coherent intensities scattered from a sample containing 50 at% Ga at different sample temperatures between 295°C and 440°C for $0.05\,\text{Å}^{-1} \leq q \leq 0.6\,\text{Å}^{-1}$. These curves are smoothed and desmeared. Upon approaching the critical temperature, which was determined to be 295.2°C, a strong increase of the scattered intensities could

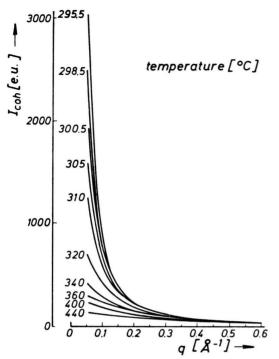


Fig. 1. Molten Cd-Ga (50 at % Ga): coherent scattered intensity at different temperatures.

be observed for $q < 0.3 \, \text{Å}^{-1}$. For $q > 0.5 \, \text{Å}^{-1}$ the shape of the scattering curves at different temperatures is nearly identical. In [14] it was shown that the scattering curves exhibit a minimum at $q \sim 0.8 \, \text{Å}^{-1}$. At this minimum value, the coherent intensity has the same order of magnitude as that from the melts of the pure elements Cd and Ga, and thus can be identified essentially as due to the density fluctuations. This contribution must be subtracted in order to obtain only the scattering due to the concentration fluctuations.

The compressibility of various liquid alloys of the Cd-Ga system was determined in [19] by means of ultrasonic velocity measurements for temperatures up to 400 °C. In this work, the temperature coefficient of the ultrasonic velocity for different alloys as well as an isotherm of the compressibility at 330 °C are reported. These results were confirmed in part 1 of this work for 1 melt with 55 at% Ga and were therefore used for the other concentrations. From this data, the scattering due to the compressibility was calculated according to Equation (5). This procedure seemed to be justified although a certain discrepancy has been detected [14]

between the compressibility data as determined by scattering experiments and by ultrasonic velocity measurements. This discrepancy was found to exist for both pure elements, Cd and Ga. However, the effect of this discrepancy on the evaluation of the scattering due to the concentration fluctuations can be neglected. Equation (5) is strictly valid only for q = 0, but may, according to [20], be applied as a good approximation for small values of q. Hence:

$$I_{\text{coh}}(q) = A \varkappa_T + B S_{\text{CC}}(q) \quad (\text{for } q \rightarrow 0). \quad (12)$$

According to Eqn. (5), $S_{\rm CC}(q)$ is expected to be a Lorentzian following the Ornstein-Zernike theory. Figures 2, 3, and 4 show the graph of $I^{-1}(q)$ as a function of q^2 (OZ plot) for some intensity curves for different concentrations, I(q) being defined as

$$I(q) = I_{\text{coh}}(q) - A \varkappa_{T} = BS_{\text{cc}}(q)$$
(13)

It appears, that the Ornstein-Zernike theory provides an adequate description of the present experimental results. The value of $S_{\rm CC}(0)$ follows from I(0). The dilatation factor, ϑ , contained in B, was calculated for each concentration from the density measurements [21]. For mean concentrations, ϑ amounts to approximately 0.15.

To achieve a complete description of the concentration fluctuations in the molten Cd-Ga system,

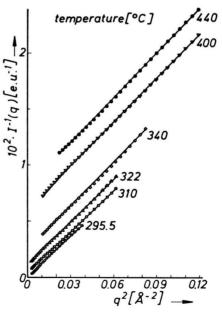


Fig. 2. Molten Cd-Ga (50 at % Ga): Ornstein-Zernike-plots.

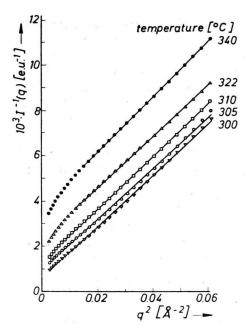


Fig. 3. Molten Cd-Ga (45 at % Ga): Ornstein-Zernike-plots.

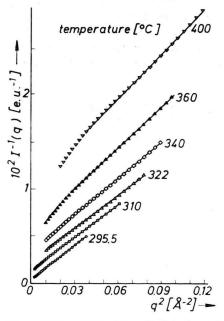


Fig. 4. Molten Cd-Ga (55 at % Ga): Ornstein-Zernike-plots.

seven binary melts were investigated at temperatures between 400 °C and the phase separation line. Each of the melts containing 20 and 80 at% Ga, respectively, were investigated at ten different temperatures. For the other melts, twenty to thirty

runs were performed at different temperatures. The OZ plots obtained at different temperatures are nearly parallel. No deviation from the OZ theory can be observed for the melts near the critical temperature. The OZ plots for temperatures more than $30\,^{\circ}\mathrm{C}$ above T_{c} show a slight deviation from linear behaviour at small q-values (see Figs. 3 and 4) as was also observed with a number of other melts in a qualitative way for $q\,\xi \leqslant 1$.

4.2. $S_{CC}(0)$

In Fig. 5 the isothermal run of $S_{CC}(0)$ versus the concentration is shown for six different temperatures. The vertical scale was chosen in such a way that the maximum $S_{CC}(0)$ -values for the two melts with 45 and 55 at% Ga at 295.5°C appear in the graph. For the melt with 50 at % Ga, $S_{CC}(0)$ reached values of approximately up to 900 upon approaching T_c . According to Fig. 5, $S_{CC}(0)$ is larger along the entire concentration range than the ideal case $(c_A c_B)$, which is indicated with a broken line. For the melts with 45 and 55 at % Ga, $S_{CC}(0)$ reaches the value of 100 $c_A c_B$, for the melts with 40 and 60 at % Ga, $S_{CC}(0)$ reaches 40 $c_A c_B$. At a temperature of $100\,^{\circ}\text{C}$ above T_{c} , $S_{\text{CC}}(0)$ lies between $2 c_A c_B$ and $5 c_A c_B$ in the concentration range between 20 and 80 at % Ga. This indicates, that segre-

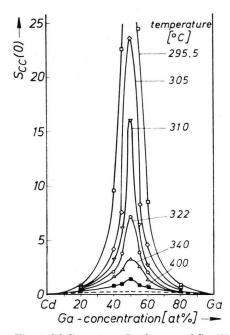


Fig. 5. Cd-Ga-system: Isothermes of $S_{\text{CC}}(0)$, --- $S_{\text{CC}}^{\text{id}}(0)$.

gation behaviour exists up to the temperature mentioned. For molten Li-Na with a nearly critical concentration, $S_{\rm CC}(0) \approx 32$ was determined in [5] for a reduced temperature $\varepsilon \approx 1.2\ 10^{-2}$. This value is comparable to $S_{\rm CC}(0) \approx 23.6$, which was obtained from Fig. 5 for the Cd-Ga melt with 50 at% Ga at $305\,^{\circ}{\rm C}$, corresponding to $\varepsilon \approx 1.8\ 10^{-2}$.

For further discussion of $S_{CC}(0)$ the following relationship is used:

$$S_{\rm CC}(0) = c_{\rm A} c_{\rm B} \left(\frac{\partial a_{\rm A}}{\partial c_{\rm B}}\right)_{\rm p, T, N}^{-1}.$$
 (14)

According to Eqn. (14), the slope of the critical activity isotherm approaches zero, as $S_{CC}(0)$ diverges at the critical point. Eqn. (14) allows the direct comparison between $S_{CC}(0)$, obtained by smallangle scattering measurements and by measurements of the activity, respectively. For the Cd-Ga system, activity data are only available for T>426°C [22]. For these temperatures, only weak small-angle scattering is observed. Furthermore, no unambigous graphical differentiation of the activity isotherm for calculating $S_{CC}(0)$ is possible. In spite of this, the various values of $S_{CC}(0)$, which can be obtained by these completely different methods show the same order of magnitude through the entire concentration range. However, the $S_{CC}(0)$ obtained from the activities are slightly larger than those obtained from the scattering data.

4.3. Correlation lengths

Figure 6 shows the correlation length ξ of the concentration fluctuations as a function of temperature and concentration. The uncertainty in the

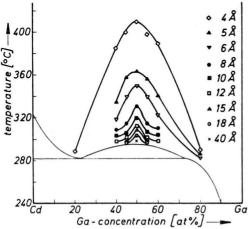


Fig. 6. Cd-Ga-system: phase diagram with lines of constant correlation length.

data amounts to less than +5%. Related to the concentration of 50 at % Ga, the behaviour of ξ is symmetrical. This fact becomes obvious especially considering the temperature dependence of ξ for the melts containing 45 and 55 at % Ga, respectively. From these results, and from the results of additional experiments near the critical point, it follows, that the critical concentration of the Cd-Ga system is approximately 50 at % Ga. The critical point cannot be evaluated precisely from the phase diagram [23] as the phase boundary line shows a very low curvature. The total enthalpy of mixing attains its maximum value at about 55 at % Ga [22]. The direct observation, by small-angle scattering, of the concentration fluctuations characterizing the critical point must be considered to be the most convenient method for the determination of the critical point.

The melt with critical concentration shows a definite divergence of ξ upon approaching T_c from higher temperatures. The maximum ξ -values observed were about 100 Å. For $T < T_c$, macroscopic segregation takes place and a sharp decrease of the measured ξ could be observed. For the 45 and 55 at% Ga melts, instead of the divergence, only a distinct maximum of ξ is detected at temperatures between T_c and the phase boundary. It should be noted that the correlation lengths, which can be determined within the two-melt region, arise from concentration fluctuations within one single phase and not from the electron density differences between the two coexisting phases. From the measured correlation lengths, the interaction time, τ , of the X-ray quanta within the correlated regions can be estimated to be $\tau < 10^{-16}$ sec. This is several orders of magnitude smaller than the characteristic relaxation time of the fluctuations (> 10^{-11} sec according to Ref. 4). Thus, the static approximation is valid. However, no information concerning the dynamic behaviour of the fluctuations is to be expected.

4.4. Experimental critical-points exponents

In this section we discuss the temperature dependence of the "critical" scattering of a melt with a critical composition. An experimental determination of the critical exponents requires an exact localization of the critical point with respect to c_c and T_c . The maximum points in the isothermal curves of $S_{CC}(0)$ or ξ versus concentration were taken as c_c . Thus, the critical concentration c_c of

the Cd-Ga system was found to be 50.0 ± 1.0 at % Ga. The critical temperature, T_c , was determined from the temperature dependent scattering of the melt with the critical concentration. Figure 7 shows the temperature dependence of $S_{CC}(0)^{-1}$ for a melt containing 50 at % Ga. From this graph, the critical temperature $T_c = 295.2 \pm 0.1$ °C was determined, which, within experimental accuracy, corresponds to the temperature of the maximum scattering. Figures 8 and 9 show the experimental ξ -values and $T/S_{\rm CC}(0)$ -values versus the reduced temperature $\varepsilon = (T - T_c)/T_c$ (temperatures in K), respectively, for a melt with c_c . Since T_c in the Cd-Ga system is relatively low compared to other metallic systems, this system can be studied over a large range of reduced temperature $(5 \cdot 10^{-4} \le \varepsilon \le 2.5 \cdot 10^{-1})$. The temperature dependence of ξ and of $T/S_{CC}(0)$, respec-

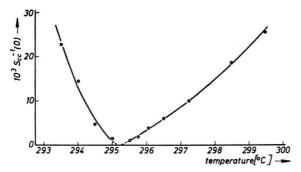


Fig. 7. Molten Cd-Ga (50 at % Ga): temperature dependence of $[S_{\rm CC}(0)]^{-1}$.

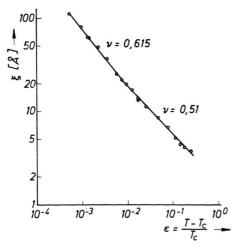


Fig. 8. Molten Cd-Ga (50 at % Ga): temperature dependence of the correlation length $\xi.$

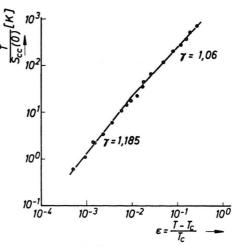


Fig. 9. Molten Cd-Ga (50 at % Ga): temperature dependence of $T/S_{\rm CC}(0)$.

tively can be described by a simple power law. A least squares fit using $T_{\rm c}=295.2\,^{\circ}{\rm C}$ yields for the whole ε -range

$$\xi = (1.52 \pm 0.05) \, \epsilon^{-(0.565 \pm 0.015)} [\text{Å}]$$
 (15)

and

$$T/S_{CC}(0) = (2.72 \pm 0.15) \, 10^{-4} \cdot \varepsilon^{-(1.142 \pm 0.025)} [K].$$
 (16)

Precise evaluation of Figs. 8 and 9 leads to a subdivision of the total range of ε into two partial ranges which overlap for ε at about $8 \cdot 10^{-3}$.

For $\varepsilon > 8 \cdot 10^{-3}$ the best linear least-squares analysis yields $\nu = 0.51 \pm 0.01$, i.e. the behaviour espected by the classical mean-field theory. Since the correlation lengths in the range $20\,\text{Å} \ge \xi \ge 3.7\,\text{Å}$ are experimentally of high accuracy, the critical exponent thus determined is of high reliability. For $\varepsilon < 8 \cdot 10^{-3}$, the temperature gradient within the specimen influences ε . Furthermore, the larger ξ -values require the observation at q-values near the experimental lower q-limit of $0.05\,\text{Å}^{-1}$. Therefore, the maximum error in the determination of the correlation lengths larger than $50\,\text{Å}$ may be assumed to be about $\pm 10\,\%$. For this reason, the critical exponent $\nu = 0.615$ for $\varepsilon < 8 \cdot 10^{-3}$ is obtained with an error of ± 0.05 .

In a similar way from the $T/S_{\rm CC}(0)$ -values of Fig. 9 one obtains in the range $\varepsilon > 8 \cdot 10^{-3} \ \gamma = 1.06 \pm 0.03$ and in the range $\varepsilon < 8 \cdot 10^{-3} \ \gamma = 1.185 \pm 0.09$.

By the present experiments, the critical exponent η proofed to be zero.

The behaviour of the Cd-Ga system for $\varepsilon > 10^{-2}$, i.e. for temperatures more than 6° C above T_c , can be described by means of the mean-fiel dtheory. Below $\varepsilon = 8 \cdot 10^{-3}$, the critical exponents, ν and ν , indicate, within the experimental accuracy, a behaviour according to the lattice-gas theory.

Critical experiments performed with liquids and melts up to now yielded different values for the critical exponents. For different organic binaries, for example, by means of light scattering, values of $1.1 \le \gamma \le 1.5$ have been obtained [24, 25]. Nevertheless, a comparison of the present exponents with the few data reported for metallic systems is of interest. For Bi-Ga, the classical exponents $\nu = 0.5$ and $\gamma = 1.0$ were reported [4]. By means of neutron scattering, for Li-Na melts in [5], values of $\nu = 0.57$ and $\gamma = 1.1$ were evaluated for $1.2 \cdot 10^{-2} \le$

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 $\varepsilon \leq 1.7 \cdot 10^{-1}$, whereas for $10^{-4} \leq \varepsilon \leq 1.5 \cdot 10^{-2}$ with the same system by means of X-ray scattering, $\nu = 0.655 + 0.03$ and $\gamma = 1.296 + 0.061$ are reported

Thus, the exponents obtained from Li-Na melts and from Bi-Ga melts are in good agreement with those obtained from Cd-Ga melts. Critical phenomena, characterized by long-range correlations, are rather insensitive to the special atomic interaction. Therefore, metallic systems as well as organic binary systems or one component fluid systems appear to follow the lattice-gas theory for $\varepsilon \to 0$. For larger ε -values, a gradual transition to the mean-field behaviour can be observed.

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