Determination of the elementary jump of Co in CoGa by quasielastic neutron scattering

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Quasielastic neutron scattering at the backscattering spectrometer IN16 at the ILL has been used to determine the elementary jump vector of diffusing Co atoms in the $B2$ phase of CoGa. Measurements have been performed on Co single crystals with 54 at. % Co and 64 at. % Co. For both compositions a maximum of the quasielastic broadening has been observed near a reciprocal lattice point corresponding to a $B2$ superlattice reflection. This gives unambiguous evidence of Co diffusion via nearest neighbor jumps. From the residence times on the antistructure sites high defect concentrations are deduced. The correlation of Co diffusion has been found to be surprisingly weak. A diffusion mechanism is suggested which takes advantage of the high degree of disorder and, therefore, cannot be described in terms of defined cycles.

I. INTRODUCTION

$B2$ structures (or CsCl structures) are derived from bcc structures via a different occupation of the two simple cubic sublattices by two types of atoms. Since self-diffusion in intermetallic $B2$ alloys is generally believed to be vacancy diffusion, the high defect concentrations found in these alloys play an important role in the diffusion process.[1] Vacancy diffusion in these compounds can be imagined in two ways: The diffusing atoms may perform jumps to nearest neighbor (NN) sites creating antistructure defects, or they may stay on their ''own'' sublattice by performing jumps to next nearest neighbor (NNN) sites. While NNN jumps are believed to be dominant in intermetallic alloys with high ordering energies, such as NiAl,[2] NN jumps have been found in the intermetallic $B2$ alloys FeAl (Ref. 3) and NiGa.[4] Extensive studies on CoGa using tracer diffusion have been performed by Bose *et al.*[5] and Stolwijk *et al.*[6,7] On the basis of upward curvatures of the Arrhenius plots of the diffusion coefficients and equal activation energies of both components obtained from measurements of the diffusivities at various temperatures and compositions, Stolwijk *et al.* proposed a coupled diffusion of Co and Ga, the so-called triple-defect mechanism: The Co atom performs two subsequent NN jumps through a divacancy which are followed by a NNN jump of a Ga atom. The intermediate state constitutes a triple defect, i.e., two vacancies on the Co sublattice and one Co antistructure atom, and is considered to be relatively stable, since triple defects seem to be the dominant type of defects in CoGa.[8–11] On the other hand, Monte Carlo simulations showed that both, the upward curvature as well as the coupling, do not necessarily require the triple-defect mechanism but can be explained by more generalized diffusion models.[12,13] However, up to now, no *direct* investigations of the diffusive jump of any constituent of the $B2$ phase of CoGa have been performed.

In this paper we present a direct observation of the jumps of Co atoms in CoGa using quasielastic neutron scattering (QNS). QNS is the only method that allows an investigation of the diffusive jump in CoGa on the atomic scale, since CoGa contains no suitable Mössbauer isotopes (Mössbauer spectroscopy being practically limited to ^{57}Fe). While neutrons are excellent as a probe for the motion of Co atoms in CoGa in terms of incoherent scattering cross sections, they have, however, one important drawback: The high neutron absorption cross section of cobalt. We have overcome this problem by growing single crystals cut as sufficiently thin and large disks. Together with long measuring times and the high flux of the backscattering spectrometer IN16 at the Institut Laue-Langevin the obtained statistics was high enough to follow the comparably slow Co diffusion in the 10^{-13} m^2/s range.

II. THEORY

The quasielastic broadening of the incoherent scattering function $S(\mathbf{Q},\omega)$ of atoms diffusing on a Bravais lattice[14] is described by

$$\Gamma(\mathbf{Q}) = \frac{1}{\tau}\left(1 - \frac{1}{n}\Sigma\right) \quad \text{with} \quad \Sigma = \sum_k \exp(-i\mathbf{Q}\mathbf{l}_k), \quad (1)$$

where Γ is the line width of the single Lorentzian which constitutes $S(\mathbf{Q},\omega)$, τ the mean residence time on a lattice site, n the number of target sites, and $\mathbf{l}_k$ a jump vector to the kth target site. In $B2$ structures this model applies to direct NNN jumps, but also to jumps via antistructure sites with negligibly short residence times on these sites. The combination of these two NN jumps can be approximated by an effective jump on the simple cubic sublattice in $\langle 100 \rangle$, $\langle 110 \rangle$ or $\langle 111 \rangle$ direction[3] (corresponding to jumps into the second, third, and fifth coordination shell). As a general rule for all such models it can be said that $\Gamma(\mathbf{Q})$ has a minimum near reciprocal lattice points of the *jump* lattice and a maximum at the boundary of its Brillouin zone.

The situation is different for NN jumps where the jump lattice is no longer a Bravais lattice.[15] For $B2$ structures $S(\mathbf{Q},\omega)$ is the sum of two Lorentzians with widths Γ_i and weights w_i:

$$\Gamma_i(\mathbf{Q}) = -M_i(\mathbf{Q}) \quad \text{and} \quad w_i(\mathbf{Q}) = \left| \sum_j \sqrt{c_j}[\mathbf{b}_i(\mathbf{Q})]_j \right|^2. \tag{2}$$

M_i and $\mathbf{b}_i$ denote the ith eigenvalue and ith eigenvector of the matrix $\mathbf{A}$ with components

$$A_{11} = -\frac{1}{\tau_{Co}}, \quad A_{12} = \frac{\Sigma}{n\,\tau_{Ga}}, \quad A_{21} = \frac{\Sigma}{n\,\tau_{Co}}, \quad A_{22} = -\frac{1}{\tau_{Ga}}, \tag{3}$$

τ_{Co} and τ_{Ga} denote the average residence times of a Co atom on a site of the Co and Ga sublattice, respectively, and c_j the Co concentration on the jth sublattice.

Still, the broadening of the total line shows a minimum near reciprocal lattice points corresponding to fundamental reflections of the $B2$ jump lattice. However, at reciprocal lattice points that correspond to superlattice reflections a considerable broadening of $S(\mathbf{Q},\omega)$ due to a maximum of intensity of the broad line can be observed. This is due to the fact that wave functions associated to scattering processes on different sublattices are no longer in phase in these directions. QNS measurements of $S(\mathbf{Q},\omega)$ near these points in reciprocal space are therefore particularly suitable to decide between NN and NNN jumps.

III. EXPERIMENT

A. Sample and sample environment

Two CoGa single crystals, one with 54 at. % Co and one with 64 at. % Co were grown using the Czochralski method. From these single crystals disks with a diameter of 25 mm and a thickness of 4 mm were cut. The large diameter allowed to take advantage of the 3×3 cm neutron beam. The disks were mounted into niobium sample holders with their rotation axes parallel to the incoming neutron beam. In order to avoid contact melting of Nb with CoGa, an Al_2O_3 fiber paper (thickness 0.5 mm) was placed between the sample and the sample holder.

Between different measurements the disks were turned around their rotation axis by an angle ζ (counterclockwise, when seen from the neutron source) in order to obtain different orientations. The orientation of the crystal lattice was determined by x-ray diffraction and was such that the $\langle 100 \rangle$ axis was in the scattering plane when $\zeta = 176°$ and $\zeta = 125°$ for $Co_{54}Ga_{46}$ and $Co_{64}Ga_{36}$, respectively. In both cases the $\langle 100 \rangle$ axis pointed into the direction $2\Theta = 155°$ (see Fig. 1). In this position the $\langle 001 \rangle$ plane was inclined relative to the scattering plane by $-45°$ ($Co_{54}Ga_{46}$) and $6°$ ($Co_{64}Ga_{36}$) around the $\langle 100 \rangle$ axis (counterclockwise seen from the origin). For both orientations the $\mathbf{Q}$ vectors with $Q = 1.77$ and 1.89 Å^{-1} come very close to the $\langle 100 \rangle$ reciprocal lattice point (see Fig. 1).
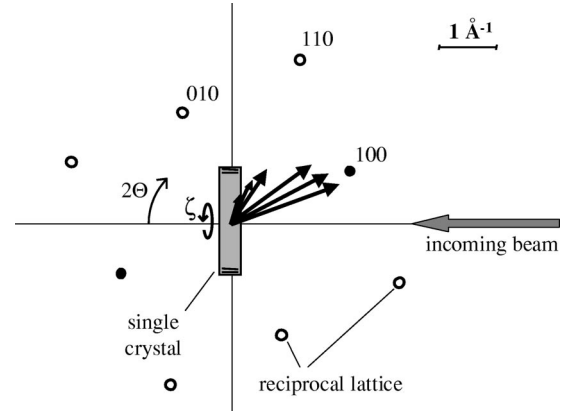

FIG. 1. Schematic representation of the orientation of the reciprocal lattice of the two samples $Co_{54}Ga_{46}$, $\zeta = 176°$, and $Co_{64}Ga_{36}$, $\zeta = 125°$, seen from above. The full circles represent reciprocal lattice points lying in the scattering plane. The points represented by empty circles are out of the scattering plane, since the $\langle 001 \rangle$ plane is inclined around the $\langle 100 \rangle$ axis. The arrows represent the scattering vectors $\mathbf{Q} = \mathbf{k}_{in} - \mathbf{k}_{out}$ in the QNS experiment at IN16. Each vector corresponds to one of the six analyzers. Please note that for two of the orientations where QNS measurements were performed, $Co_{54}Ga_{46}$, $\zeta = 184°$, and $Co_{64}Ga_{36}$, $\zeta = 125°$, in each case two $\mathbf{Q}$ vectors are very close to a $\langle 100 \rangle$ reciprocal lattice point which corresponds to a $B2$ superlattice reflection.

B. Measurement

The measurements have been performed at the backscattering spectrometer IN16 at ILL using the unpolished Si-$\langle 111 \rangle$ analyzers. In this setup a Gaussian shaped resolution with a full width at half maximum (FWHM) of about 0.9 μeV is obtained. The neutron wavelength is 6.27 Å. We used six single ^{3}He-detectors counting neutrons collected by the analyzers at $2\Theta = 30°$, $50°$, $69°$, $106°$, $125°$, and $141°$ covering a Q range from 0.5 to 1.9 Å^{-1}. The Doppler frequency of the monochromator was 4 Hz and hence an energy range from -4.1 to 4.1 μeV could be covered.

The exact resolution functions have been measured at room temperature using a nickel disk with the same dimensions as the CoGa single crystals. The Gaussian shape of the resolution function is especially convenient for the detection of Lorentzians exhibiting weak quasielastic broadening. This is due to the different shape at the wings of these two curves. In order to determine the background, measurements with the empty sample holder as well as with the sample holder containing a cadmium disk have been performed. These measurements indicate that the main part of the background was *not* caused by the sample environment behind the sample, which incited us to perform no absorption correction and subtract the background as a whole. Some channels suffered from comparably high background (especially $2\Theta = 50°$ between -3.0 and -0.7 μeV, but also $2\Theta = 30°$, $69°$, and $106°$ all between -4.1 and -3.5 μeV) and were discarded from the fits in the final data evaluation.

The recently installed diffraction multidetector at IN16 allowed to scan for possible Bragg peaks from the Al_2O_3 paper, but no such peaks were detected. The first Bragg peak
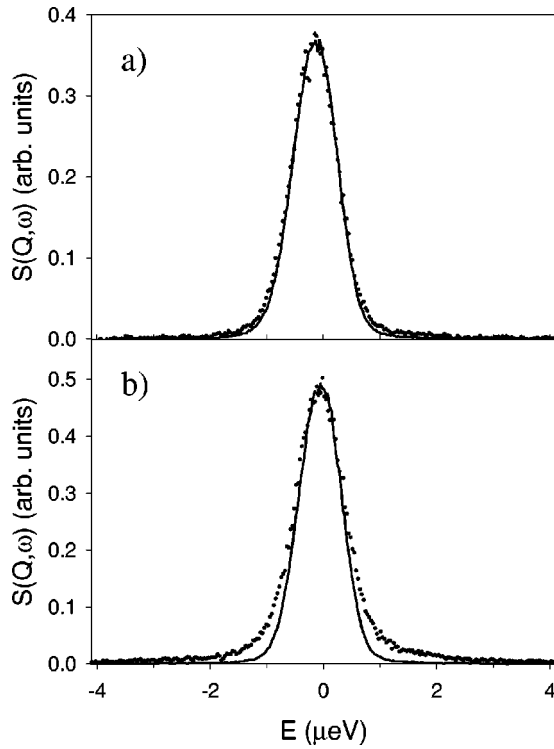
FIG. 2. QNS spectra taken at $Q = 0.52$ Å^{-1} (a) and 1.78 Å^{-1} (b) on the Co$_{64}$Ga$_{36}$ single crystal in the orientation $\zeta = 125°$. The solid lines represent the resolution functions (scaled to maximum). Counting time: 20.5 h.

FIG. 3. Comparison of line widths obtained by a fit of Co$_{54}$Ga$_{46}$ (a) and Co$_{64}$Ga$_{36}$ (b) assuming a quasielastic line broadening in form of a single Lorentzian. The lines show the calculated widths for NNN-jumps (solid) and jumps to the third (long dashed) and fifth (short dashed) coordination shell.

of the sample itself is expected at $Q = 2.17$ Å^{-1} and therefore out of the experimental Q range. Multiple scattering could be neglected because of the short average neutron path length due to high absorption. The strong difference in the incoherent neutron scattering cross sections of the two components ($\sigma_{inc}^{Co} = 4.8$ b, $\sigma_{inc}^{Ga} = 0.16$ b) allowed to study the Co diffusion without a noticeable interfering signal of the Ga atoms.

Sample measurements were performed on the single crystal with 54 at % Co at 1120 °C with $\zeta = 55°$ and 184 ° and on the single crystal with 64 at % Co at 1130 °C with $\zeta = 125°$, 235 °, and 330 °. The average counting time per orientation was 20 h. Figure 2 shows two typical spectra. For two of the orientations the vector of the momentum transfer **Q** for $2\Theta = 125°$, and 141 ° came very close to the $\langle 100 \rangle$ reciprocal lattice point (Fig. 1). These orientations were $\zeta = 184°$ for the Co$_{54}$Ga$_{46}$ and $\zeta = 125°$ for the Co$_{64}$Ga$_{36}$ single crystal.

IV. RESULTS

For all fits the quasielastic lines calculated on the basis of different jump models were numerically folded with the measured resolution function. In the following we concentrate on the two orientations given in Fig. 1, since they allow a very clear decision between different models.

A. Fit with models based on Bravais jumps

The spectra have first been refined with a single Lorentzian as predicted for jumps on a Bravais lattice [Eq. (1)].
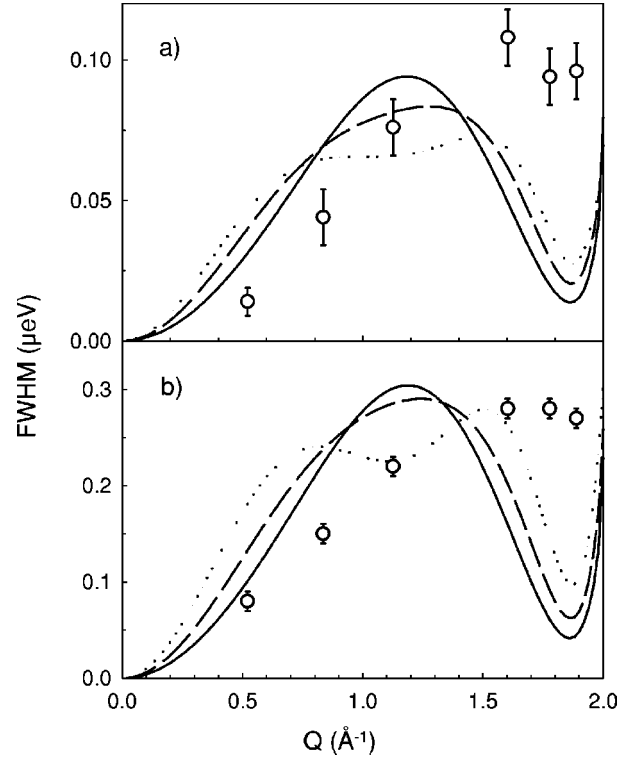
Figure 3 shows the so obtained linewidths for the two orientations described in Fig. 1, in comparison to the linewidths calculated on the basis of various models assuming jumps on a Bravais lattice. All these models have in common a pronounced minimum of the line width at the higher Q values. However, the line widths obtained with a single line fit show a *maximum* at this position (Fig. 3). The experimental contradiction to these models is also obvious from Fig. 2: While the Bravais models predict a *similar* line broadening for $Q = 0.52$ Å^{-1} and $Q = 1.78$ Å^{-1} [Fig. 3(b)], there is a pronounced difference in the quasielastic broadening of the two experimental spectra. Therefore, jumps to NNN sites, but also jumps into the third and fifth coordination shell have to be discarded.

B. Fit with jumps to antistructure sites

The strong broadening at the high Q values for the two orientations described in Fig. 1 can easily be explained by the presence of a second, broader line [Eqs. (2) and (3)] resulting from jumps of Co atoms to antistructure sites where the residence time has to be shorter than on the Co sites.[4] Since the data did not allow a free fit of a single spectrum with two Lorentzians (mainly due to the convolution with the resolution function which tends to smear out the difference in the line shapes of a single Lorentzian and the sum of two Lorentzians), we proceeded as follows:

The spectra with the highest quality corresponding to $2\Theta = 125°$ and 141 ° have been fitted *simultaneously* for all
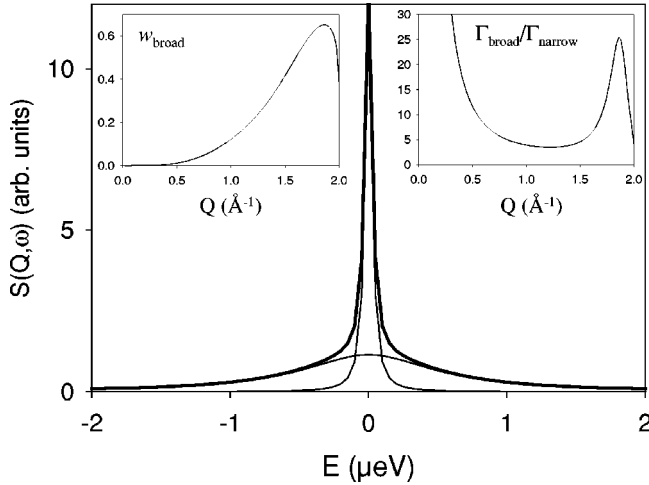
FIG. 4. Lorentzians as fitted for $Co_{64}Ga_{36}$, $\zeta = 125°$ at $Q = 1.88$ Å^{-1} before the convolution with the resolution function. Thin lines: Broad and narrow Lorentzians. Thick lines: Sum. Inset left: Q dependence of the relative weight of the broad line. Inset right: Ratio of line widths of the broad and the narrow Lorentzians (Both insets for $Co_{64}Ga_{36}$, $\zeta = 125°$). The proportion of the two Lorentzians can be determined from the values given in the insets at $Q = 1.88$ Å^{-1}.

orientations of each sample on the basis of the NN-jump model Eqs. (2) and (3). The model dependent fitting parameters were the diffusion constant and the ratio τ_{Ga}/τ_{Co}. We obtained $\tau_{Ga}/\tau_{Co} = 0.29(5)$ for 64 at. % Co. For 54 at. % the χ^2 dependence was very flat, probably due to the smaller line broadening. A local minimum of χ^2 was detected at τ_{Ga}/τ_{Co} 0.16(5). A second minimum was found at 0.24, however, this value was discarded, since it corresponds to unprobably high defect concentrations.

In a second step, in order to show that the obtained results are consistent with all measured spectra, each spectrum was refined individually by coupling a broad line to a narrow line with a ratio of weights and linewidths calculated according to Eqs. (2) and (3) on the basis of the τ_{Ga}/τ_{Co} values obtained with the simultaneous fit. The free parameter was the linewidth of the narrow line. Figure 4 shows a fit with two coupled Lorentzians assuming a ratio of the residence times τ_{Ga}/τ_{Co} of 0.29. The comparison of the fit results with the calculated widths is shown in Fig. 5. The agreement is excellent. This is due to the fact that a broad line resulting from jumps to antistructure sites has been taken into account. From this we conclude that the Co atoms perform NN jumps to and from Ga sites.

C. Defects

Using the detailed balance $\tau_{Ga}/\tau_{Co} = c_{Co}^{\beta}/c_{Co}^{\alpha}$, we get a concentration of antistructure Co atoms $c_{Co}^{\beta} = 0.074(20)$ for $Co_{54}Ga_{46}$ at 1120 °C and $c_{Co}^{\beta} = 0.146(20)$ for $Co_{64}Ga_{36}$ at 1130 °C, referred to the number of lattice sites. Vacancy concentrations have been calculated from c_{Co}^{β} according to Neumann *et al.*[16] assuming that triple defects are the dominant defect type.[8–11] We obtain $c_V = 0.067(40)$ for $Co_{54}Ga_{46}$ at 1120 °C and $c_V \approx 0.008$ for $Co_{64}Ga_{36}$ at 1130 °C, again
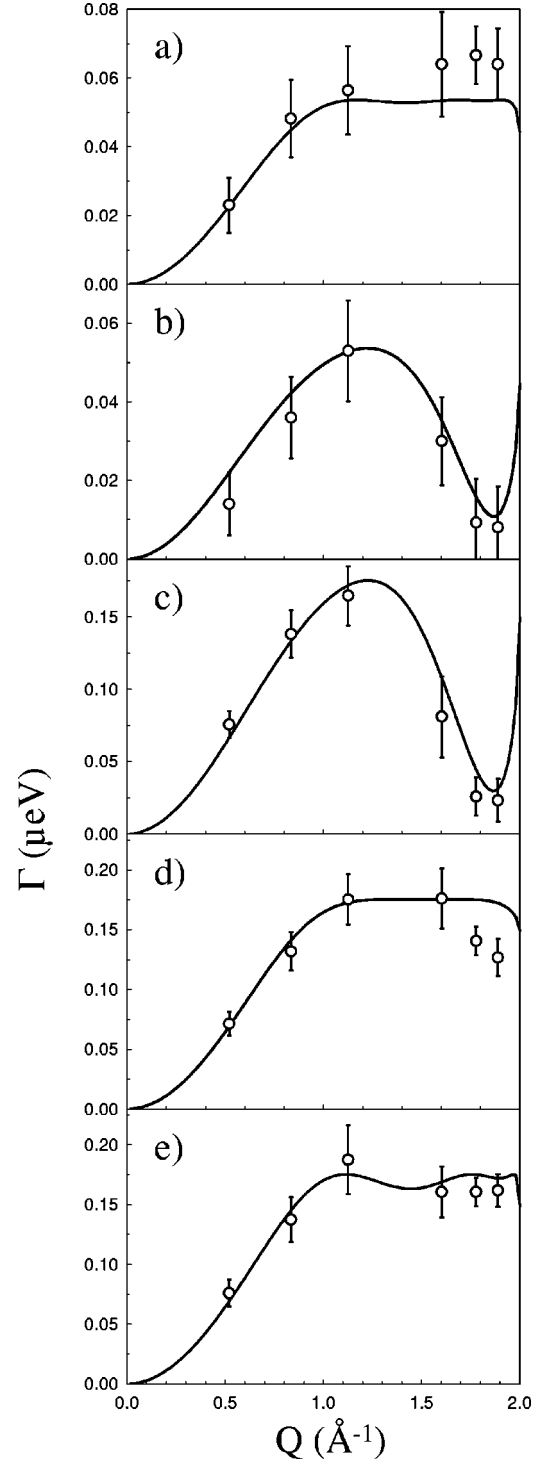

FIG. 5. Comparison of widths of the narrow lines predicted by the NN jump model ($\tau_{Ga}/\tau_{Co} = 0.16$ and 0.29, D_{Co} as given in Sec. IV D) with those obtained experimentally (fit with coupled widths) for $Co_{54}Ga_{46}$, $\zeta = 55°$ (a) and $184°$ (b) as well as for $Co_{64}Ga_{36}$, $\zeta = 125°$ (c), $235°$ (d), and $330°$ (e).

referred to the number of lattice sites. These high vacancy concentrations appear reasonable in the context of studies on the defect concentrations in CoGa at lower temperatures[10,17–20] where vacancy concentrations at stoichiometry up to 5% (at 900 °C) have been found.[10]

D. Diffusion constants and correlation factors

In this section we propose a direct access to correlation factors which otherwise can only be determined indirectly by means of the isotope effect. This is done by comparing long range diffusivities with individual jump frequencies.

According to[21]

$$D_{\mathrm{Ni}} = \frac{a^2}{4(\tau_{\mathrm{Ga}} + \tau_{\mathrm{Co}})}, \qquad (4)$$

the diffusion constants obtained in the QNS experiment are $D_{\mathrm{Co}}^{\mathrm{QNS}} = 0.73(15) \times 10^{-12}$ m^2/s for Co$_{54}$Ga$_{46}$ at 1120 °C and $D_{\mathrm{Co}}^{\mathrm{QNS}} = 2.15(20) \times 10^{-12}$ m^2/s for Co$_{64}$Ga$_{36}$ at 1130 °C. Please note that Eq. (4) does not contain the correlation factor[22] f, defined as the ratio of the mean square displacement of an atom after a large number of jumps with and without correlation,

$$f = \frac{\langle \mathbf{R}^2 \rangle}{\langle \mathbf{R}_{\mathrm{random}}^2 \rangle}. \qquad (5)$$

Therefore, with a given jump length, the D^{QNS} depend only on the jump frequencies, since they have been fitted in the Q range from 1.77 to 1.89 Å^{-1} which reflects the atomic motion on the Å scale. On the other hand the diffusion constants from tracer experiments contain inherently the correlation factor since they are obtained from long range diffusion. This allows to estimate f from a comparison of diffusion constants obtained by the two methods

$$f = \frac{D^{\mathrm{tracer}}}{D^{\mathrm{QNS}}}. \qquad (6)$$

There are no values from tracer experiments for exactly 54 at. % Co, that is why we have interpolated the data of Stolwijk *et al.*[7] and get $D_{\mathrm{Co}} \approx 0.68 \times 10^{-12}$ m^2/s at 1120 °C for 54 at.% Co. Since the diffusion constants obtained by the two methods are similar the correlation factor must effectively be close to unity. Taking into account the uncertainties of our measurements and the interpolation of the tracer data we get a lower limit for f_{Co} of about 0.65. This result is supported by the fact that for both samples there is a good agreement of the line broadenings predicted by the (long range diffusion) model with those measured at high Q values (sensitive to local motion) *as well as* at small Q (sensitive to long range diffusion). Figure 6 shows the Q dependent linewidths calculated according to the hydrodynamic limes

$$\Gamma = 2\hbar D Q^2 \quad \text{for } Q \to 0, \qquad (7)$$

assuming D^{QNS} multiplied by $f = 0.5$ and $f = 1$. A comparison with the linewidths at 0.5 Å^{-1} limits the correlation factor f_{Co} in Co$_{54}$Ga$_{46}$ to values between 0.5 and 1.0.

For Co$_{64}$Ga$_{36}$ a determination of f_{Co} from a comparison of the diffusion constants is not possible due to the absence of tracer diffusion data. However, the linewidths at small Q which are fairly consistent with the uncorrelated model (Figs. 5 and 6) indicate that f_{Co} is at least as close to unity as for 54 at. % Co$_{54}$Ga$_{46}$. An overview is given in Table I.
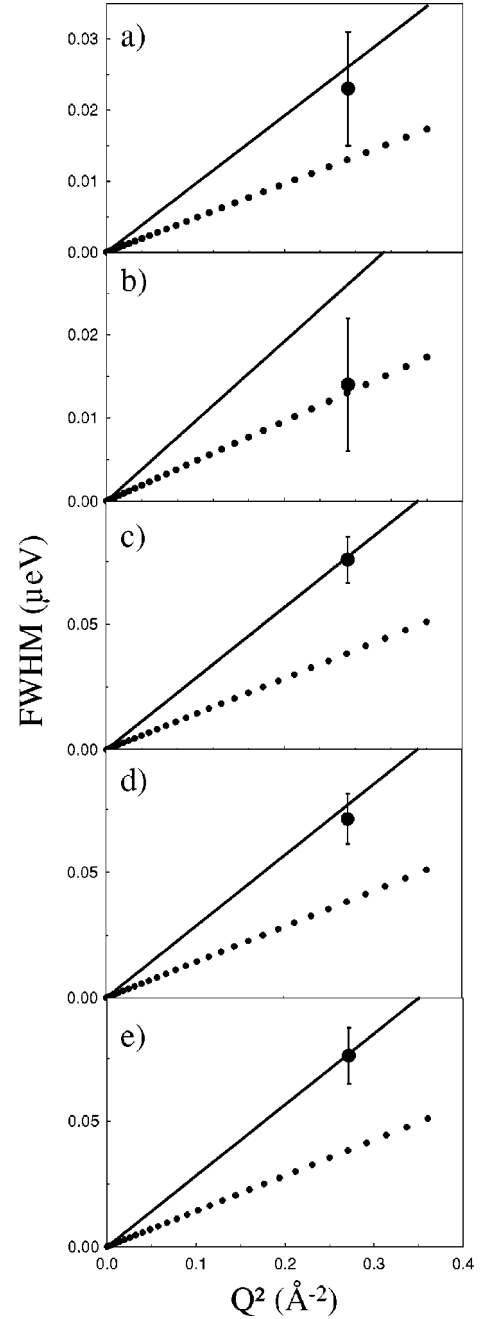

FIG. 6. Thick lines: The hydrodynamic limes in the range of its approximate validity assuming a diffusion constant that is the product of D^{QNS} obtained at high Q and a correlation factor $f = 1.0$ (solid) and $f = 0.5$ (dotted). Thin line: NN jump model. The letters (a)–(e) indicate the same single crystal orientations as given in Fig. 5. The Q range between 0 and 0.6 Å^{-1} is rather influenced by macroscopic diffusion than by the microscopic diffusion. The linewidth at $Q = 0.52$ Å^{-1} can therefore be taken as a reference for the macroscopic diffusion constant. Obviously, there is no deviation towards smaller line widths [exept for (b) which can be attributed to statistical deviations] which indicates that f is close to unity. The two orientations (a) and (b) of the Co$_{54}$Ga$_{46}$ sample are well described by a correlation factor $0.5 < f \leq 1$, the three orientations (c), (d), and (f) of the Co$_{64}$Ga$_{36}$ single crystal indicate a correlation factor of at least 0.7.

TABLE I. Diffusion constants according to the QNS and tracer experiments (interpolation of the data of Stolwijk *et al.*) as well as correlation factors *f* as determined from a comparison of the QNS and tracer diffusion constants (fourth column) and from the linewidths at $Q = 0.52$ (fifth column).

sample	$D^{QNS}(m^2/s)$	$D^{tracer}(m^2/s)$	f from D^{tracer}/D^{QNS}	f from linewidths
54 at. % Co at 1120 °C	$0.74(15) \times 10^{-12}$	0.72×10^{-12}	$0.65 \leqslant f \leqslant 1$	$0.5 \leqslant f \leqslant 1$
64 at. % Co at 1130 °C	$2.15(20) \times 10^{-12}$	-	-	$0.7 \leqslant f \leqslant 1$

E. Conclusions on the diffusion mechanism

Since the QNS experiment shows that Co diffuses via antistructure sites we will concentrate on mechanisms based on Co NN jumps as there are the six-jump cycle (6JC), the anti structure bridge mechanism (ASB) and the triple-defect mechanism (TDM).

The *six-jump cycle*[23] has been proposed by Bose *et al.*[5] as a possible diffusion mechanism in CoGa. It consists of six subsequent jumps, where the first three jumps lower the degree of order while the consecutive jumps restore the order to its initial level. The importance of this mechanism for highly ordered stoichiometric alloys is uncontested and this mechanism permits under certain circumstances a correlation factor close to unity for one of the components.[24] However, as has been pointed out by Kiguchi and Sato,[25] this mechanism is not relevant for systems where the degree of order is sufficiently low to allow the temporary persistence of locally disordered regions. Such a deviation from perfect order is clearly present in CoGa at elevated temperatures.[10,26]

Another model assuming NN jumps of Co atoms is based on diffusion via *antistructure bridges* (ASB).[27] According to Monte Carlo simulations this mechanism cannot contribute to long range diffusion as long as the concentration of antistructure atoms is smaller than 13 %.[28] This is clearly the case for the near stoichiometric composition investigated in the present paper. However, we can exclude this mechanism also for the far-off stoichiometric composition for the following reason: If the ASB mechanism would be effective beyond the percolation threshold and only be limited by an insufficient number of antistructure atoms at the near stoichiometric compositions, there would nevertheless remain jumps on small, nonpercolating ''ASB islands.'' This would lead to an additional elastic line at small Q values due to the confined diffusion and in addition to a smaller correlation factor for the near stoichiometric composition. However, such an effect has not been observed in the QNS experiment. On the contrary, the data for both compositions can be fitted with a model based on long-range diffusion as has been shown in Sec. IV B.

The triple defect model has been proposed by Stolwijk *et al.*[7] to explain the coupled activation energies of Co and Ga diffusion obtained in tracer diffusion measurements at numerous temperatures and compositions ranging from 45.2 to 60 at. % Co. In this model the Co atoms perform jumps through divacancies being limited to their actual unit cell until a Ga atom moves one of the two vacancies to an adjacent unit cell by means of a NNN jump. The activation energies of both components are then coupled, since the *net* diffusion of Co is strongly coupled to the diffusion of Ga. The differences in the jump frequencies of Co and Ga can be compensated by different correlation factors.[29] Yet, if the Co atoms performed numerous NN jumps in their unit cell ''waiting'' for the Ga atom to free the divacancy, these jumps would not contribute to net diffusion and the correlation factor should therefore be considerably lower for Co than for Ga (Fig. 7).

Taking into account the weak correlation for Co diffusion found in the QNS experiment, the triple-defect mechanism appears only possible under the assumption that the jump frequencies for *individual* NN jumps of Co are smaller or comparable to the frequencies of NNN jumps of Ga atoms. This would mean that the energy barrier for Co NN jumps would not be lower than the one for Ga NNN jumps. In the light of the easiness at which Co antistructure atoms form in CoGa (Ref. 30) this, however, seems improbable.

A possible solution can be found in a mechanism which takes advantage of the high degree of disorder and is therefore not restricted to the maintenance of perfect local order as long as the overall degree of order is preserved. This mechanism could be either based on NN jumps of *both* components or NN jumps of Co and NNN jumps of Ga—without, however, requiring the strict binding of two vacancies and therewith the coupling of the diffusion of the two components. At a first glance both models appear to contradict the results of Stolwijk *et al.*, but—as Monte Carlo simulations have shown—also a diffusion mechanism based on NN jumps of both components is able to account for the
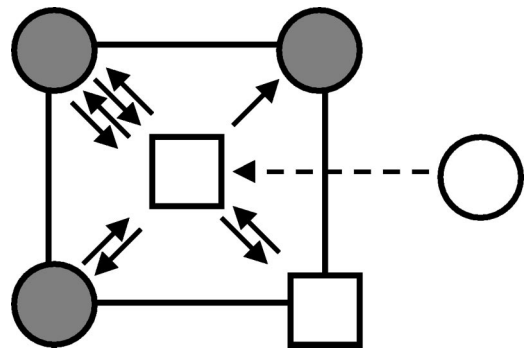

FIG. 7. Schematic representation of a *B*2 unit cell in two dimensions. The sites at the corner of the square are assumed to be part of the Co sublattice, the center of the square represents a regular Ga site. Co atoms are symbolized by full circles, Ga atoms by open circles and vacancies by empty squares. The arrows symbolize atomic jumps according to the triple-defect mechanism: The Co atoms perform numerous jumps in the unit cell until a Ga atom from an adjacent unit cell ''frees'' the divacancy by performing a NNN jump. This leads to a low correlation factor for Co diffusion if NN jumps of Co are more frequent than NNN jumps of Ga atoms (Ref. 13).

upward curvature of the tracer diffusion coefficient[12] and the coupling of the two components.[13]

A more generalized diffusion mechanism is also suggested by a comparison with similar results on NiGa (Ref. 4), where all models based on strictly defined diffusion cycles failed to explain the experimental data. The correlation factors close to unity found in the experiment could be quite naturally be explained by a difference of the atomic interactions E_{Co-Co} and E_{Ga-Ga}. This has been shown by Kikuchi and Sato using the path probability method[25,31] and later by different authors using Monte Carlo simulations.[32] In both cases very high values for the correlation factors have been found for one of the components as a consequence of a difference in the respective atom-atom interactions. Such an asymetry is realized in CoGa where antistructure atoms of Co form much easier than of Ga antistructure atoms.[11] This effect might be further enhanced by the high vacancy concentrations found in the investigated systems.

In addition, recently performed Monte Carlo simulations[33] assuming high vacancy concentrations indicate that the path of the diffusing atoms in NiGa is influenced by second and third-nearest neighbor interactions between vacancies and atoms—a phenomenon that has already been observed in Monte Carlo simulations on FeAl (Ref. 34) assuming a single vacancy. Further these simulations show, in combination with QNS measurements, that the differences in the microscopic diffusion mechanism observed in FeAl and NiGa can be explained by differences in atom-vacancy interactions solely and do not require principally different diffusion cycles. In this context we suggest that details of diffusion in CoGa are determined by atom-vacancy interactions in the second and third coordination shell while an asymmetry of the Co-Co and the Ga-Ga interactions accounts for a correlation factor close to unity for Co diffusion.

V. SUMMARY

Quasielastic neutron scattering (QNS) on the backscattering spectrometer IN16 at ILL has been used to determine the diffusive jump of Co in CoGa. For both investigated compositions (54 and 64 at. % Co) a maximum of the quasielastic broadening has been observed near a reciprocal $\langle 100 \rangle$ lattice point. This can only be explained by the presence of a second, broader Lorentzian arising from jumps to antistructure sites. If this second Lorentzian is taken into account in the data treatment (via a coupling to the smaller Lorentzian in the refinement) a good agreement between experiment and theory is achieved. The elementary jump of Co in CoGa has therefore been identified as a *nearest-neighbor* jump between regular Co sites and antistructure sites.

On the basis of a comparison of the line broadening at high Q values with the line broadening at low Q as well as with diffusion constants from tracer measurements, a correlation factor for Co diffusion not smaller than approximately 0.65 was found. Hence, Co diffusion in CoGa appears to be surprisingly effective in terms of long range diffusion compared to frequencies of individual jumps. With regard to this weak correlation, the triple-defect mechanism can only be operative in CoGa under the assumption that the energy barrier for nearest-neighbor jumps of Co atoms is at least as high as the one for next-nearest-neighbor jumps of Ga atoms, which seems improbable in the light of the unusually high concentrations of Co antistructure atoms that can be found in CoGa.

We suggest a diffusion mechanism which takes advantage of the high degree of disorder present in the investigated system and can therefore not be described in terms of defined cycles. The high correlation factor for Co diffusion probably originates in an assymetry of the atom-atom interactions.

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