Chainlike hydrogen ordering in α-ScD$_x$ systems

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Hydrogen ordering is investigated in the α-ScD$_x$ system for two concentrations $x=0.19$ and $x=0.33$ by diffuse neutron-scattering techniques. The results reveal the formation of chains, consisting of pairs of hydrogen atoms located on second-neighbor tetrahedral interstitial sites along the hexagonal direction. The results are similar to those found previously in α-LuD$_x$. The differences between α-ScD$_x$ and α-LuD$_x$ give evidence for a chain formation due to a lowering of coherency stresses.

I. INTRODUCTION

The phase diagram of some rare-earth–hydrogen systems such as ScH$_x$, YH$_x$, HoH$_x$, ErH$_x$, TmH$_x$, and LuH$_x$ is characterized by a solid-solution phase extending to rather high hydrogen concentrations and stable down to 0 K.[1] An anomaly in resistivity found ten years ago in α-LuH$_x$ was the first indication for some structural change occurring within the solid solution.[2] Recently, a diffuse neutron-scattering experiment on LuD$_{0.19}$ revealed ordering characteristics of hydrogen atoms on their tetrahedral interstitial sites within the hexagonal metal lattice.[3] The scattering pattern of LuD$_{0.19}$ shows at 150 K essentially a two-dimensional intensity distribution, i.e., intensity ridges perpendicular to the hexagonal axis, and therefore gives evidence for a chainlike arrangement of hydrogen atoms parallel to the hexagonal directions. Moreover, localized intensities were observed, indicating the presence of interchain correlations. It was shown that the individual chain consists of pairs of hydrogen atoms located on second-neighbor tetrahedral sites along the c axis, with a metal atom in between. In order to get agreement with the experimental data it was necessary to assume that the chains show a displacement step after each consecutive hydrogen pair. This zig-zag arrangement explains the Q-space modulation of the diffuse intensity observed. For LuD$_x$ we argued that the long-range characteristics of the hydrogen arrangement, i.e., the chain length of about 3–4 hydrogen pairs together with the interchain correlations, are determined by a lowering of coherency energies of this linear structure within the cylindrical elastic symmetry of the hexagonal metal matrix. On the other hand, it remains an open question whether the individual pair formation is essentially of elastic or electronic origin. For lutetium, the observation of a split-hydrogen local mode[4] in the ordered state indicating the presence of a direct D-D interaction favors an electronic explanation. However, some elastic interaction is not excluded, and the undisplaced central

metal atom in the paired state is a strong indication for at least an elastic contribution to the pair formation. Qualitatively similar results on hydrogen ordering were also obtained for α-YD$_{0.19}$ but the authors[5] interpreted their data by a purely one-dimensional ordering of pairs along the hexagonal axis. In order to get further insight into the ordering properties of rare-earth–hydrogen systems, we have investigated in the present work α-ScD$_x$ crystals at two hydrogen concentrations.

ScD$_x$ was chosen for the following reasons: First, Sc, although in the hcp structure too, has, when compared to Lu, some different structural and elastic properties, e.g., a smaller unit cell, a bigger ratio of the lattice constants c and a, and a different elastic anisotropy. Furthermore, Sc behaves differently than Lu under hydrogen absorption, i.e., the Sc lattice expands with increasing hydrogen concentration more strongly within the basal plane, whereas Lu shows a higher lattice expansion along the hexagonal direction. Secondly, the solid-solution phase of ScD$_x$ extends towards higher hydrogen concentration, i.e., $x=0.35$ (Ref. 6) at room temperature and below and allows therefore an easier investigation of hydrogen ordering as a function of concentration. The present study will further corroborate the importance of elastic interactions in the formation of the chainlike arrangement. The paper is organized as follows. In Sec. III we present the diffuse scattering data for ScD$_{0.19}$ and ScD$_{0.33}$. Section IV deals with an analysis of the scattering pattern and its consequences for the ordering process.

II. EXPERIMENT

The measurements were done on the triple-axis spectrometer VALSE located at a cold-neutron guide position of the Orphée reactor of the Laboratoire Léon Brillouin, Saclay. The spectrometer was operated in the elastic mode at a neutron wavelength of 0.236 nm. In order to eliminate second-order contamination, a pyrolitic graph-

ite filter was used in the incident beam. The collimations were about 30'.

The single crystals of ScD$_{0.19}$ and ScD$_{0.33}$, loaded with deuterium from the gas phase, had a mosaic width of about 60'. The measurements were done in a closed-cycle cryostat. From 300 down to 130 K, wide regions of the (c^*,a^*) reciprocal-lattice plane were scanned, up to the (004) and the (200) reciprocal-lattice points.

III. RESULTS

A. The ScD$_{0.19}$ system

The measurements were done at different temperatures between 300 and 130 K. The latter temperature is well below the resistivity anomaly of 160 K. Figure 1(a) shows the intensity difference between 130 and 300 K, plotted as a full width at half maximum contour. The figure exhibits diffuse intensity ridges perpendicular to the c^* axis and intersects it near the $(0\,0\,\frac{4}{3})$ and $(0\,0\,\frac{8}{3})$ positions, respectively. Similar to the results for LuD$_x$, the diffuse ridges show a curvature, i.e., a wavelike modulation in reciprocal space with a (200) periodicity. In contrast to the results for LuD$_{0.19}$, the present data on ScD$_{0.19}$ show a somewhat broader width of the diffuse ridges along the c^* axis. Moreover, a closer look at the data shows that the intersection points with the c^* axis are somewhat shifted from the commensurate positions, i.e., the first-order streak intersects near a (0 0 1.3) point and the second-order streak reaches the c^* axis near a (0 0 2.7) point.

Furthermore, the figure shows localized intensities, depicted by closed contours, near the same positions as previously observed in LuD$_{0.19}$.[3]

The temperature dependence of the scattering pattern was investigated between 130 and 300 K. At higher temperatures the intensity decreased (Fig. 2), but the shape of the diffuse ridges remained nearly unchanged. Only the width of the intensity distribution along c^* was increased by about 20% at room temperature. Moreover, the temperature dependence of the localized intensities, at higher temperatures similar to that of the ridges, showed below 200 K a drastic increase (Fig. 2) connected with a narrowing of the localized distribution by about 20%.

B. The ScD$_{0.33}$ system

The intensity difference between 130 and 300 K is shown in Fig. 1(b) for the ScD$_{0.33}$ crystal. Individual

FIG. 1. (a) Difference between the diffuse scattering intensities observed at 130 and 300 K within the (c^*,a^*) plane in ScD$_{0.19}$. The bars are not error bars but indicate the full width at half maximum of the intensity distributions observed in individual scans. The dashed lines are guides to the eyes. (b) Difference between the diffuse scattering intensities observed at 130 and 300 K within the (c^*,a^*) plane in ScD$_{0.33}$. The symbols are the same as in (a).

FIG. 2. Temperature dependence of the diffuse intensities in ScD$_{0.19}$. The points are average values obtained from different reciprocal-lattice positions. Open triangles, intensities of the streaks; solid squares, localized intensities.

FIG. 5. Localized intensities for $ScD_{0.33}$ as shown in a scan along the $\Gamma-K-M$ direction at 200 and 140 K respectively. Open squares, 200 K; solid circles, 140 K.
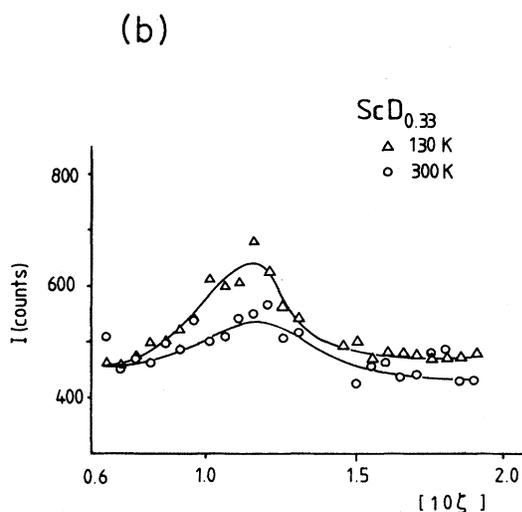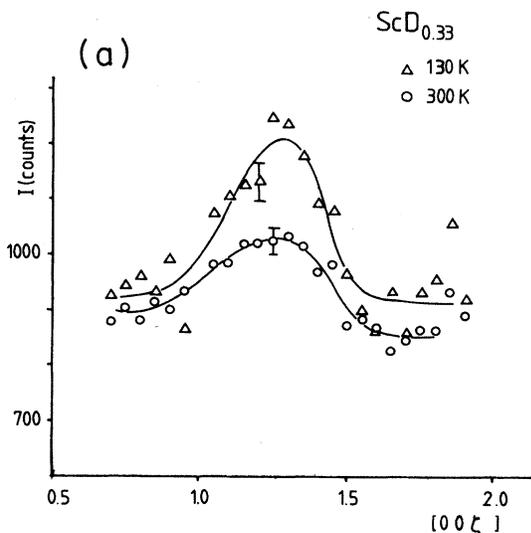
FIG. 3. (a) Diffuse elastic scan along the hexagonal $[00\zeta]$ direction in $ScD_{0.33}$. Triangles, 130 K; circles, 300 K. (b) Diffuse elastic scan along the $[10\zeta]$ direction in $ScD_{0.33}$. The symbols are the same as in (a).
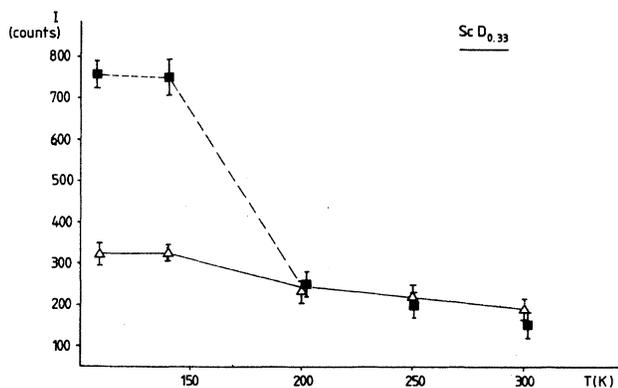
FIG. 4. Temperature dependence of the diffuse intensities in $ScD_{0.33}$. Open triangles, intensities of the streaks; solid squares, localized intensities.

scans along the $[00\zeta]$ and $[10\zeta]$ directions are shown in Fig. 3. A scattering pattern very similar to that found in $ScD_{0.19}$ and previously in $LuD_{0.19}$ is observed. This time, however, the intersection points of the diffuse streaks with the c^* axis are shifted still further away from the commensurate positions, i.e., scans along the c axis show maxima now near the $(0\,0\,1.25)$ and $(0\,0\,2.75)$ reciprocal-lattice positions, respectively.

In $ScD_{0.33}$ the temperature dependence of the diffuse ridges gave qualitatively a similar result as in $ScD_{0.19}$ and $LuD_{0.19}$, i.e., an intensity decrease (Fig. 4) connected with a broadening of the ridges along c^* at higher temperatures. Moreover, the temperature dependence of the localized intensities shows in $ScD_{0.33}$ below 200 K a similar drastic increase, but even more pronounced than in $ScD_{0.19}$. This intensity increase (Fig. 5) connected with a peak narrowing indicates the presence of correlations of longer range.

IV. ANALYSIS OF THE SCATTERING PATTERN

Both ScD_x crystals investigated show a diffuse intensity distribution similar to that observed previously in $LuD_{0.19}$.[3] Diffuse intensity ridges perpendicular to the c^* axis and intersecting it near the $(0\,0\,\frac{4}{3})$ and $(0\,0\,\frac{8}{3})$ positions were observed. The ridges exhibit a wavelike pattern in q space with a (200) periodicity. Moreover, localized intensities were found near the same reciprocal-lattice positions as in $LuD_{0.19}$. In ScD_x, however, the localized intensities show below 200 K a drastic intensity increase together with a narrowing in q-space, indicating a transition to an ordered state with correlations of longer range. This last behavior was not observed in $LuD_{0.19}$.

In view of the qualitative similarity of the scattering data for $LuD_{0.19}$, $ScD_{0.19}$, and $ScD_{0.33}$, it seems that hydrogen ordering can be described by a common structural model for all three systems investigated. The basic structural units describing hydrogen ordering are chains consisting of pairs of hydrogen atoms located on second-neighbor tetrahedral interstices along the c direction.

The chains show a displacement step after each consecutive pair. This linear hydrogen arrangement explains the two-dimensional characteristics of the scattering pattern and reproduces the intersection of the diffuse ridges with the c^* axis near the $(0\,0\,\frac{4}{3})$ and $(0\,0\,\frac{8}{3})$ reciprocal-lattice positions. The zig-zag configuration of pairs within a chain is needed in order to explain the streak curvature in reciprocal space. Indeed, any straight arrangement of hydrogen pairs along the same c axis will always induce intensities lying in a plane perpendicular to c^* and consequently will not produce the streak curvature observed. Moreover, the localized intensities found in all three systems indicate that interchain correlations should be taken into account. The main features of the scattering pattern can be reproduced by a mean configuration of parallel adjacent chains, There are three different configurations for this chain arrangement. First, the two chains may be in phase, or the two chains may be out of phase by $\pm c$, respectively. The calculated scattering pattern obtained from a statistical average of the three possible two-chain arrangements, taking into account all symmetry operations of the hexagonal lattice, is in quite good agreement with the experimental results (Fig. 7). The calculations reproduce the variation of the intensity ridges in q space and also exhibit the localized intensities observed.

Despite different lattice properties, essentially the same structural model applies for both LuD$_x$ and ScD$_x$ systems. The results yield both metals and all three concentrations the same mean interchain distance $b = a\sqrt{3}$, suggesting an interchain repulsion of the same nature in all three cases. This argument is further corroborated by the following considerations. In ScD$_{0.19}$ and ScD$_{0.33}$, the diffuse streaks are broader along the c axis than in LuD$_{0.19}$ (20%) and therefore the chains are shorter. If the chains are shorter in ScD$_x$ at the same hydrogen concentration, it follows that more chains are present in the ordered state in ScD$_{0.19}$ and consequently in ScD$_{0.33}$. The higher number of parallel chains, however, does not

FIG. 7. Calculated full width at half maximum contours of the scattered intensity within the (c^*,a^*) plane obtained from a statistical average of the three structures shown, taking into account all symmetry operations of the hexagonal matrix. For the regions of increased intensity marked by dashed contours, no reliable experimental data are available for comparison due to the nearby Bragg peaks.

change the mean interchain distance, which therefore seems to be a minimum distance. Furthermore, the higher chain density in the ordered state leads to an increased contribution of interchain interference effects to the scattering pattern. Especially at low temperatures, the increase of the localized intensities shows a tendency towards a chain arrangement with correlations of longer range between the chains.

Moreover, the increased interchain correlation is also reflected in the small displacement of the intersection points of the diffuse ridges with the hexagonal axis from the commensurate $(0\,0\,\frac{4}{3})$ and $(0\,0\,\frac{8}{3})$ positions. Considering the scattering along c^*, the structural amplitude for an isolated chain is given as

$$A(Q) = \sum_{n=0}^{N} e^{iQnd} \ ,$$

where d is the projection of the hydrogen-hydrogen distance on the c axis and N is the number of atoms in a chain. If now a second chain is added in an out-of-phase configuration, then along the c^* direction the structure amplitude for the two chains is written as

$$F(Q) = (1 + e^{iQ(c/4)})A(Q) = (1 + e^{iQ(c/4)}) \sum_{n=0}^{N} e^{iQnd} \ ,$$

FIG. 6. Three different two-chain arrangements on adjacent c axes along the b direction. Full squares, D atoms; open squares, empty T sites; circles, metal atoms.

where c means the lattice constant in the hexagonal direction. The phase shift between the two chains $e^{iQ(c/4)}$ induces a cosine modulation in reciprocal space along c^* with maxima at $Q=(0\,0\,0)2\pi/c$ and $(0\,0\,4)2\pi/c$ and with a minimum in between at $Q=(0\,0\,2)2\pi/c$.

This modulation induces a small shift of the maxima of $F(Q)$, i.e., the maxima of $A(Q)$ along c for $Q=2\pi/d$ and $Q=4\pi/d$ are shifted somewhat in $F(Q)$ towards the $(0\,0\,0)$ and $(0\,0\,4)$ points, respectively.

It follows that if within the ensemble of interchain configurations the interchain interference increases, due to a higher number of individual chains, a shift of the diffuse ridges towards the $(0\,0\,0)$ and $(0\,0\,4)$ points should be expected. In agreement with these considerations this shift was found in $ScD_{0.19}$ and appears to be more pronounced in $ScD_{0.33}$.

V. DISCUSSION

The present ScD_x results show that similar to LuD_x hydrogen ordering can be described by the formation of chainlike structures along the hexagonal direction, showing interchain correlations. The main difference to LuD_x seems to be that in ScD_x the hydrogen chains are shorter, consequently increasing the interchain interference effects. Moreover, the ScD_x system shows at low temperatures and higher hydrogen concentrations a tendency towards the formation of a long-range arrangement of parallel chains. Together with the previous results on $LuD_{0.19}$ the present investigation further shows that the chain configuration is characterized by a minimum interchain distance, indicating a repulsive interaction between the chains. If hydrogen pairs are described as elastic dipoles, the orientation of these dipoles is fixed within the hexagonal metal matrix and parallel to the c axis. The chain formation then would correspond to an ordering of the elastic dipoles governed by a lowering of coherency stresses in the hexagonal matrix. Khachaturyan[7] has generally discussed the formation of linear precipitates within a metal matrix. Coherent linear structures are favored by a degeneracy of elastic energies in two dimensions as being the case in hexagonal systems. The chainlike arrangement of elastic dipoles lowers the coherency energy in this system of cylindrical elastic symmetry. Consequently, the same mean interchain distance observed in $LuD_{0.19}$, $ScD_{0.19}$, and $ScD_{0.33}$ may be seen as the minimum distance between hydrogen pairs still allowing a cylindrical symmetry in the hydrogen arrangement. The ordering of elastic dipoles should also depend on the elastic anisotropy of the metal matrix. The LuD_x system is elastically softer than ScD_x along the c direction as borne out by the longitudinal elastic constants and also by the hydrogen-induced lattice-parameter change. In

qualitative agreement with this, the experiment shows longer hydrogen chains in LuD_x than in ScD_x.

Finally, we should comment on the question of whether the individual pair formation is of electronic or elastic origin. The observation of a split local mode in LuD_x and YD_x shows the presence of a direct deuterium-deuterium interaction in the paired state of these systems. Within a pair, the hydrogen atoms are separated by a metal atom in between, and consequently this interaction is probably mediated by the conduction electrons. The split local mode in LuD_x and YD_x therefore indicates the presence of an electronic interaction between the hydrogen atoms. This, however, does not necessarily mean that this electronic interaction is responsible for the pair formation. Moreover, a recent neutron-scattering experiment on ScD_x (Ref. 8) gives no evidence for a split-hydrogen local mode, although, as shown in this work, the main characteristics for hydrogen ordering are similar to those observed in LuD_x and YD_x. Therefore, the local-mode splitting and consequently a direct D-D interaction is not a necessary precondition of hydrogen ordering. On the other hand, the explanation of pair formation due to a gain of elastic energy—i.e., the metal atom between the hydrogen atoms is not displaced at all—essentially based on symmetry arguments is valid for all hcp rare-earth–hydrogen systems.

Recently an extensive investigation of the local-mode properties in $YD_x(H_y)$ by Anderson et al.[9] has shown that the local-mode splitting is strongly concentration dependent and disappears at lower concentrations $(x \sim 0.06)$. The authors deduced from these observations a concentration-dependent ordering tendency and claimed for the disappearance of the $\frac{3}{4}c$ pair at low concentrations. It is too early at present to comment precisely on this interpretation for $YD_x(H_y)$. A careful investigation of hydrogen ordering at low concentrations by elastic diffuse neutron scattering would be necessary. The results, however, for ScD_x from both elastic and inelastic measurements show that the local-mode splitting is not a necessary signature of the pair formation and therefore cannot be taken generally as a characteristic measure for the evolution of the ordered state.

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[1]For a review see J. P. Burger, J. N. Daou, A. Lucasson, P. Lucasson, and P. Vajda, Z. Phys. Chem. (Neue Folge) **143**, 111 (1985).

[2]J. N. Daou, A. Lucasson, and P. Lucasson, Solid State Commun. **19**, 895 (1976).

[3]O. Blaschko, G. Krexner, J. N. Daou, and P. Vajda, Phys. Rev. Lett. **55**, 2876 (1985); O. Blaschko, G. Krexner, J. Pleschiutschnig, J. N. Daou, and P. Vajda, Phys. Rev. B **39**,

5605 (1989).

[4]O. Blaschko, G. Krexner, L. Pintschovius, P. Vajda, and J. N. Daou, Phys. Rev. B **38**, 9612 (1988).

[5]I. S. Anderson, J. J. Rush, T. Udovic, and J. M. Rowe, Phys. Rev. Lett. **57**, 2822 (1986); J. E. Bonnet, D. K. Ross, D. A. Faux, and I. S. Anderson, J. Less-Common Met. **129**, 287 (1987); M. W. McKergow, D. K. Ross, J. E. Bonnet, I. S. Anderson, and O. Schaerpf, J. Phys. C **20**, 1909 (1987).

[6]J. N. Daou, P. Vajda, A. Lucasson, and J. P. Burger, Phys. Status Solidi A **95**, 543 (1986).

[7]A. G. Khachaturyan, *Theory of Structural Transformations in Solids* (Wiley, New York, 1983).

[8]O. Blaschko, J. Pleschiutschnig, L. Pintschovius, J. P. Burger, P. Vajda, and J. N. Daou, Phys. Rev. B **40**, 907 (1989).

[9]I. S. Anderson, N. F. Berk, J. J. Rush, and T. J. Udovic, Phys. Rev. B **37**, 4358 (1988).