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Hydrogen ordering in α-LuD$_x$ investigated by diffuse neutron scattering

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Hydrogen ordering in the solid-solution phase of LuD$_x$ is investigated by diffuse-neutron-scattering techniques. The results show a linear ordering tendency of hydrogen atoms forming chains along the hexagonal *c* direction. Within the chains, second-neighbor tetrahedral sites are occupied. The scattering pattern in both the c^*-a^* and c^*-b^* reciprocal-lattice planes gives evidence for interchain correlations.

I. INTRODUCTION

The phase diagrams of several rare-earth–hydrogen systems such as ScH$_x$, YH$_x$, HoH$_x$, ErH$_x$, TmH$_x$, and LuH$_x$ exhibit some peculiar features. The solid-solution α phase remains stable even at temperatures near absolute zero and the formation of the cubic β phase occurs only at rather large hydrogen concentrations[1] (20 at. % H in the case of lutetium).

Within the solid-solution phase the hydrogen atoms occupy the tetrahedral interstices of the hcp lattice. Anomalies in macroscopic quantities such as resistivity and specific heat, however, indicated the presence of some structural changes occurring at lower temperatures.[2] Recently the present authors presented the first results of a neutron-scattering experiment revealing characteristic features of hydrogen ordering within the anomaly temperature range.[3]

Measurements within the first Brillouin zone in LuD$_{0.19}$ gave essentially a planar diffuse intensity distribution and were interpreted by a chainlike arrangement of D atoms located on second-neighbor sites along the direction of hexagonal symmetry, but forming a displacement step between two adjacent D pairs. Meanwhile, experimental data on YH (D)$_x$ have been published in two papers.[4,5] The scattering patterns presented exhibit some similarity to those found in LuD$_{0.19}$,[3] but were interpreted by a purely one-dimensional ordering of pairs along the hexagonal axis. Furthermore, recent investigations of the hydrogen local modes, first in YD$_{0.18}$ (Ref. 6) and then in LuD$_{0.19}$,[7] revealed a strong vibrational anisotropy in these systems. For Lu the frequency measured along the *c* direction is lower by about 40% than that observed in the *a* direction. In both substances, at low temperatures a splitting of the local-mode energy level was found along the *c* direction, indicating a direct D-D interaction and confirming the hydrogen-pair formation.

In the present paper we describe neutron-scattering results on LuD$_x$, investigating wide regions of reciprocal space for two scattering planes. Most of the measurements were performed on LuD$_{0.19}$, but some results were also obtained using a LuD$_{0.04}$ sample. The experiment confirms the basic structural features previously described,[3] but allows a more detailed insight into the hydrogen-ordering process occurring in this system.

II. EXPERIMENTAL

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 contaminations a pyrolytic graphite filter was used in the incident beam. The collimations were about 60′. The sample was a single crystal of lutetium with a mosaic spread of 30′ which was loaded with deuterium at 500 °C. The crystal was mounted into a closed-cycle cryostat. The LuD$_x$ system was investigated at two deuterium concentrations, i.e., LuD$_{0.19}$ and LuD$_{0.04}$.

III. DIFFUSE SCATTERING RESULTS

A. The c^*-a^* plane in LuD$_{0.19}$

The measurements were done by a series of scans in reciprocal space extending to the (004) point along the c^* direction and the (200) reflection along the a^* direction. The sample was investigated at 150 K, which is below the temperature range where the resistivity anomaly occurs, and then for comparison at 300 K. The intensity difference between the two temperatures was evaluated and the results are shown in Fig. 1.

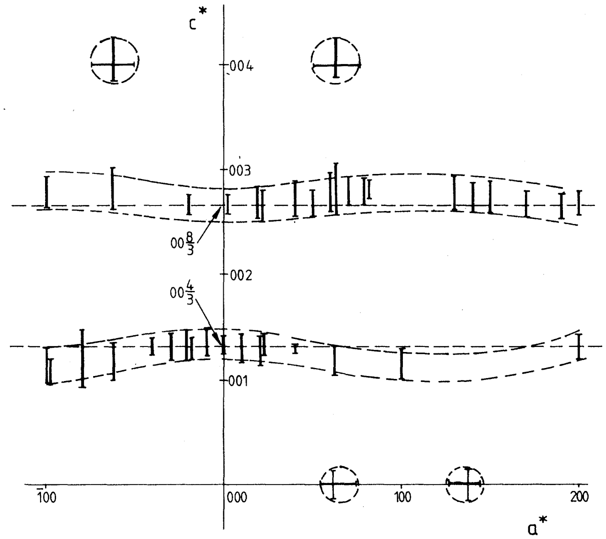

FIG. 1. Difference between the diffuse scattering intensities observed at 150 and 300 K within the c^*-a^* plane in $LuD_{0.19}$. The bars indicate the full widths at half maximum of the intensity distributions observed in individual scans, which are plotted in order to characterize the extension of the diffuse ridges. We emphasize, however, that they do not represent error bars. The positions of the center of each distribution are well defined and exhibit a significant wavelike deviation from the dashed straight lines $c^*=\frac{4}{3}$ and $\frac{8}{3}$, respectively. The dashed-contours are guides to the eyes.

The figure shows a complicated intensity pattern whose essential features can be characterized as follows. First, in accordance with the previous communication[3] a diffuse intensity ridge is observed perpendicular to the c^* direction and intersecting it near $(0,0,\frac{4}{3})$. Near the second-order position, i.e., $(0,0,\frac{8}{3})$, a similar intensity distribution is found. Secondly, both diffuse ridges show a curvature in the scattering plane, inducing a wavelike pattern for the intensity contours. Furthermore, in addition to the streaks, localized diffuse scattering patterns are found which are shown by closed intensity contours in Fig. 1. Their maxima are located near the reciprocal lattice positions (0.65,0,0), (1.35,0,0), (0.65,0,4), and $(-0.65,0,4)$; their intensity is about the same as the one observed for the diffuse ridges.

The temperature dependence of the intensity pattern was investigated by measurements at 200, 250, and 300 K, respectively. The temperature increase induces an intensity reduction (Fig. 2) for the entire scattering pattern, but even at 300 K all characteristics of Fig. 1 could still be found. Besides the intensity reduction, the scattering distribution of Fig. 1 appears somewhat widened (30% at 300 K) parallel to c^*, thus showing a decrease of correlation lengths at higher temperatures.

B. The c^*-b^* plane in $LuD_{0.19}$

The intensity difference between 150 and 300 K is shown in Fig. 3. Again, intensity ridges perpendicular to c^* are observed, intersecting the hexagonal axis near the $(0,0,\frac{4}{3})$ and $(0,0,\frac{8}{3})$ points, respectively. This time the streaks are rather flat, but still suggest some deviation from a straight line perpendicular to c^* whose curvature, however, has the opposite sign in comparison to the one observed in the c^*-a^* plane. Again, localized spots of about the same intensity are found lying near the (0,1,0) and (0,1,4) reciprocal-lattice positions (we use a rectangular coordinate system with $b=a\sqrt{3}$).

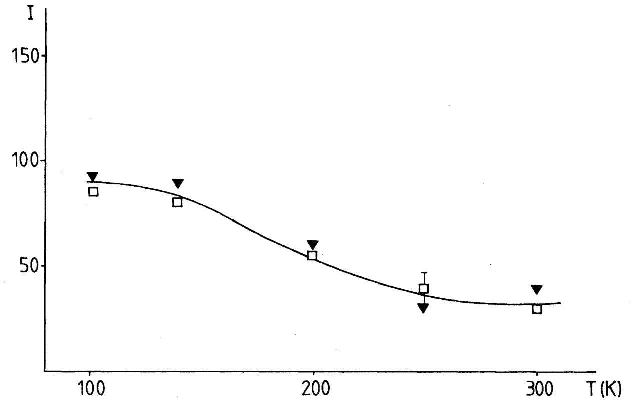

FIG. 2. Temperature dependence of diffuse intensities in $LuD_{0.19}$. The points are average values obtained from different reciprocal-lattice positions in Fig. 1. Open squares, localized intensities; solid triangles, intensities of the streaks.

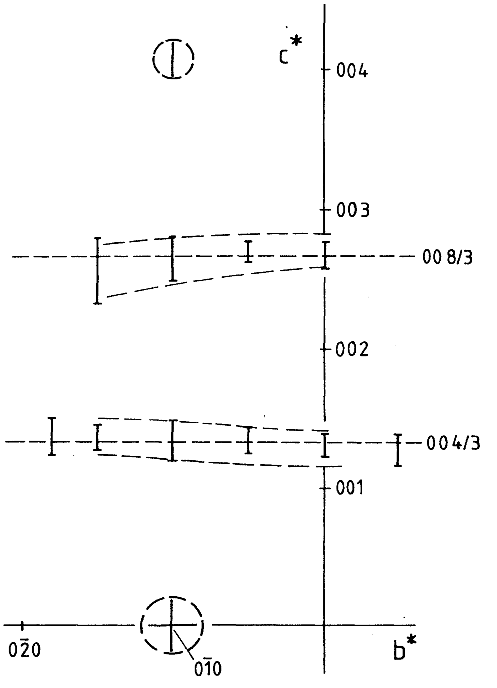

FIG. 3. Diffuse intensity difference between 150 and 300 K within the c^*-b^* plane in $LuD_{0.19}$. Symbols are the same as in Fig. 1.

C. The c^*-a^* plane in LuD$_{0.04}$

Using the same method as was used for the high concentration, the low-concentration LuD$_{0.04}$ sample was investigated at 150 and 300 K. Due to the low hydrogen content the scattering intensity was very low and, therefore, the measurements were restricted to the reciprocal-space region where the first-order ridge was observed in LuD$_{0.19}$. The results are depicted in Fig. 4 and show again a diffuse intensity distribution perpendicular to c^*. Here, however, the width along c^* is broader than in the higher-concentration system. In view of the larger width of the distribution no precise statement on the **q**-space modulation of the diffuse ridges can be made. In addition, time effects in the diffuse scattering were observed at 150 K. After 24 h at 150 K the intensity of the scattering pattern shown in Fig. 4 had increased by about 100% in comparison with the results obtained within the first 12 h. Such a time dependence was not observed in LuD$_{0.19}$.

IV. ANALYSIS OF THE SCATTERING PATTERN

The diffuse scattering in LuD$_{0.19}$ reveals intensity ridges being perpendicular to the hexagonal c^* direction and intersecting it at the $(0,0,\frac{4}{3})$ and $(0,0,\frac{8}{3})$ reciprocal-lattice positions, respectively. The ridges exhibit a wave-like pattern in **q** space with different curvature in the two scattering planes. The two-dimensional nature of this part of the scattering confirms the basic conclusion as to a linear arrangement of D atoms. The intersection points of the diffuse ridges with the c^* axis yield a periodicity of $\frac{3}{4}c$ along the hexagonal axis in real space. Furthermore, the observed width of the intensity streaks shows that the length of the linear structure in real space equals 3–5 times the distance $\frac{3}{4}c$.

On the other hand, any straight linear arrangement, e.g., a straight chain of D atoms on a c axis, will always induce a plane intensity distribution perpendicular to c^* and consequently will not be able to explain the curvature of the streaks observed. The flexure, therefore, indicates some atomic correlation perpendicular to c, inherently absent in a straight configuration.

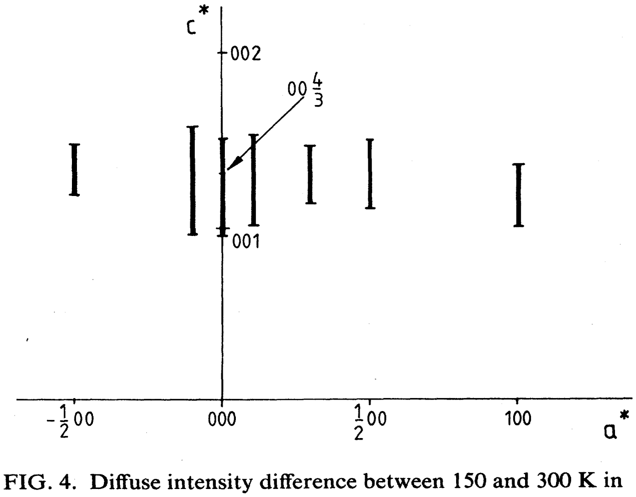

FIG. 4. Diffuse intensity difference between 150 and 300 K in the c^*-a^* plane in LuD$_{0.04}$. Symbols are the same as in Fig. 1.

In our previous communication[3] we presented a chain-like structure consisting of pairs of D atoms located on second-neighbor interstitial sites along c with displacement steps between consecutive pairs (Fig. 5). This structure gives the correct intensities on the c^* axis and also exhibits some correlation perpendicular to c. The present results, however, show additional localized intensities in both scattering planes. These intensities cannot be explained by isolated chains of D atoms as in Fig. 5 or a random arrangement of such chains, but must be attributed to the presence of interchain correlations. Indeed, the intensity spot along b^* at $(0,\bar{1},0)$ (Fig. 3) indicates a mean interchain distance of $b=a\sqrt{3}$ [the intensity spot along a^* near (0.65,0,0) corresponds to the projection of b into the a direction].

The scattering patterns in both the a^*-c^* and b^*-c^* planes exhibit a periodicity along c^* described by the (004) reciprocal-lattice vector, which corresponds to the distance $\frac{1}{4}c$ between two neighboring interstitial lattice planes along the hexagonal direction.

V. MODEL CALCULATIONS

For the reasons outlined above, we think that a chain with displacement steps after each hydrogen pair (Fig. 5) comprises the basic structural elements necessary to describe the experimental data. Yet it is obvious that uncorrelated chains of D-atom pairs oriented along the c axis cannot account for the localized diffuse intensity spots, nor can they show the $\frac{1}{4}c$ periodicity revealed by the scattering pattern.

An arrangement of two chains, however, located on two different hexagonal axes as shown in Fig. 6, gives rise to interference effects. One single chain has a wavelength of $\lambda=3c$ (in a projection on the c axis the periodicity is $\frac{3}{4}c$) and Fig. 6 shows that there are three different two-chain configurations: the two chains may be in phase [Fig. 6(a)] or the two chains may be out of phase by $\pm c$, respectively [Fig. 6(b) and 6(c)]. We have calculated the scattering-intensity distribution resulting from the configurations shown in Fig. 6, taking into account all symmetry operations of the hexagonal lattice. It turns out that the calculated scattering pattern obtained from a statistical average of the three possible two-chain arrangements is in quite good agreement with the experimental results. The calculation yields a variation of the intensity ridges in **q** space as indeed observed in the two scattering planes. Moreover, the localized intensities are also well reproduced (Fig. 7).

VI. DISCUSSION

The calculations show that configurations of adjacent chains of D atoms along c describe satisfactorily the short-range-order characteristics leading to the scattering pattern. The interchain correlations are intrinsically taken into account. The calculation further shows that the different chain configurations are distributed at random. Within our chain model the in-phase configuration has a statistical weight of $\frac{1}{3}$, whereas the two symmetrically equivalent out-of-phase arrangements contribute with a statistical weight of $\frac{2}{3}$. On the average the probability of occurrence is the same for all three configurations shown in Fig. 6.

From the temperature dependence of the diffuse scattering in $LuD_{0.19}$ one can conclude that the correlations between the chains are still present at 300 K and that disordering occurs by a shortening of the chain lengths. This is in good agreement with the conclusions drawn from an investigation of the hydrogen local modes (Ref. 7), which has shown that a considerable part of hydrogen atoms in $LuD_{0.19}$ remains in the paired state even at room temperature. Furthermore, the results for $LuD_{0.04}$ indicate that at lower concentrations, essentially individual D pairs are formed and it is not surprising that this condensation into pairs is diffusion controlled in the dilute system, as shown by the intensity changes over long times.

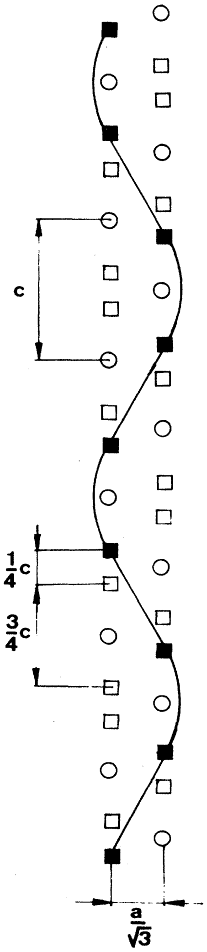

FIG. 5. Individual chain of D atoms (solid squares) on second-neighbor tetrahedral interstices with a displacement step after each D pair (from Ref. 3). Open squares, empty *T* sites; circles, metal atoms.

In our previous communication[3] we argued that the pair formation along the *c* axis was favored by a lowering of the distortion energy, since the formation of hydrogen pairs surrounding a metal atom compensates the stresses upon the latter and lowers the distortion energy when compared to a statistical distribution of single H atoms. This argument is still valid. However, in contrast to Ref. 3, which was based on restricted scattering data, in the present calculations the agreement with experiment was obtained without any displacement of the D atoms from their tetrahedral sites. Any shift of the D atoms greater than $0.01c$ away from or towards the central metal atom reduces the agreement with the experimental data, though smaller displacements of D atoms may still be present.

A comparison between the Lu-H and Y-H systems can be summarized as follows.

(a) Diffuse elastic scattering data for the a^*-c^* plane in Y-H,[4,5] though less complete, appear to be very similar to those obtained for Lu-H. In particular, the curvature of the diffuse ridge is discernible and also one of the localized intensity spots can be identified in the scattering data of Ref. 5. This has been noticed by the authors; however, it was not pursued further and was completely neglected in the construction of their model. On the other hand, the interpretation furnished in the present work accounts well for these features. On the whole, the experimental evidence from elastic diffuse scattering is in good mutual agreement for Lu-H and Y-H and, therefore, the same model should apply to both systems.

(b) Both in Y-H and in Lu-H there exists convincing evidence that a considerable amount of pairing is present even at temperatures far beyond the anomaly range between 150 and 200 K. In Y-H, using diffuse elastic measurements, the proportion of hydrogen atoms bound in pairs was estimated to be about 33% at 390 K (Ref. 4) and slightly above 40% at 350 K.[5] An estimate based on the behavior of the hydrogen local modes[6] gave about 33% at 240 K, and, also, the most recent inelastic experi-

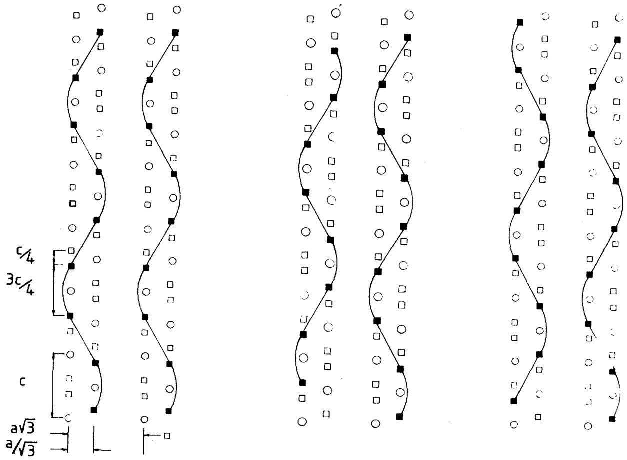

FIG. 6. Three different two-chain arrangements on adjacent *c* axes along the *b* direction.

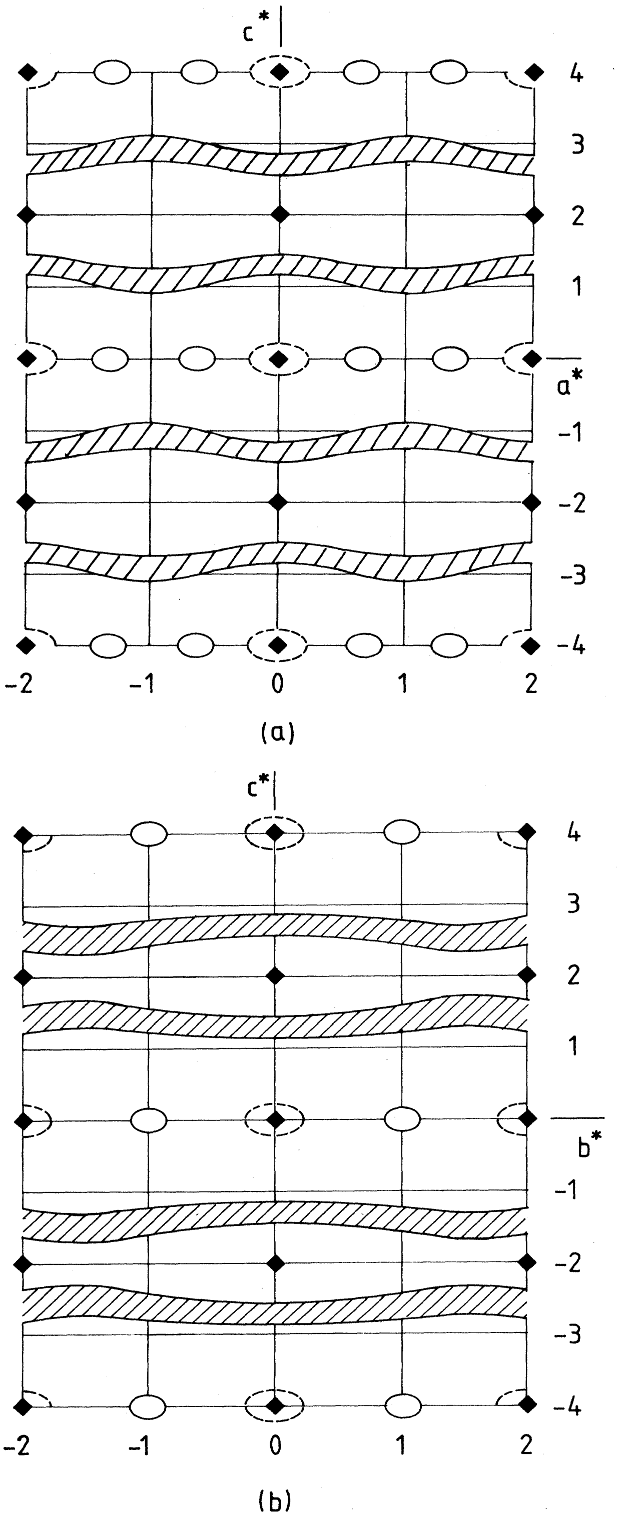

FIG. 7. Calculated full width at half maximum contours of the scattering intensity obtained from a statistical average of the three structures shown in Fig. 6, taking into account all symmetry operations of the hexagonal matrix. For the regions of increased scattering intensity marked by dashed contours, no reliable experimental data are available for comparison, due to the nearby Bragg peaks. (a) The c^*-a^* plane; (b) the c^*-b^* plane.

ment on Y-H (Ref. 8) appears to be compatible with this value. While we think that it is too early to present exact figures, we definitely conclude from our own data (both elastic and inelastic) that in Lu-H a considerable amount (maybe one-third) of the hydrogen atoms can be found in the paired state at room temperature. This shows that in both systems the effectiveness of the pairing mechanism extends to rather high temperatures.

(c) The concentration dependence of the hydrogen local modes was investigated in Y-H (Ref. 8) and the results were taken as evidence for a breakdown of pairing at low hydrogen concentrations. On the other hand, our elastic diffuse scattering data in LuD$_{0.04}$ show that, although the correlations between pairs obviously decrease strongly at low concentrations, the pairing mechanism itself is not affected. This seemingly establishes a difference in the behavior of Y-H and Lu-H at low hydrogen concentrations. We believe, however, that there may exist alternative explanations, particularly in view of the time effects observed for the low-concentration LuD$_{0.04}$ sample in the present work and also suggested for Y-H in Ref. 8. We, therefore, prefer to leave this question open until an investigation of the elastic diffuse scattering in low-concentrated Y-H has been performed.

In summary, D ordering in LuD$_x$ is described by an arrangement of chains consisting of D pairs along the hexagonal axis. The basic ingredients for this peculiar chain arrangement are determined essentially by two experimental facts. First, the displacement step between adjacent pairs within a chain is needed in order to reproduce the wavelike intensity pattern which excludes any straight atomic configuration. Secondly, the localized diffuse spots observed determine a mean distance $b=a\sqrt{3}$ between the chains. Agreement with experiment was finally obtained by a statistical average of chains over all possible sites of the interstitial lattice, taking into account the two above requirements. The tetrahedral interstitial sites form two sublattices with hexagonal symmetry within the metal lattice and the model described shows that in the ordered state both sublattices are on the average equally occupied.

Finally, it should be pointed out that the formation of chains creates a configuration of cylindrical elastic symmetry in accordance with the hexagonal symmetry of the Lu metal lattice. The long-range characteristics of the structures described may therefore be due to a lowering of coherency stresses in this cylindrical arrangement. However, at least the formation of individual pairs may be due to an electronically induced interaction, as possibly indicated by the results of the local-mode experiment.[7]

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