Electronically phase-separated charge-density waves in $Lu_2Ir_3Si_5$

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(Received 4 January 2011; published 26 April 2011)

We report the investigation of charge density waves (CDW's) in $Lu_2Ir_3Si_5$ by electron diffraction and dark-field imaging in transmission electron microscopy using superlattice diffraction spots. The CDW state is confirmed by the presence of superlattice reflections. Most interestingly, the CDW state at low temperatures is found to be electronically phase separated, with the coexistence of CDW domains and low-temperature normal phase domains. With a change in temperature, unlike other typical incommensurate CDW systems in which commensurability varies with temperature, we find that commensurability remains unchanged in the present case and that the predominant change is in the redistribution of the area ratio of the two coexisting phases, which is clearly revealed in the dark-field images obtained from the CDW superlattice reflections. The electronic phase separation in the CDW state of $Lu_2Ir_3Si_5$ is unprecedented in CDW systems, and its temperature dependence is also anomalous.

DOI: 10.1103/PhysRevB.83.155121 PACS number(s): 71.45.Lr, 64.70.Rh, 68.37.Lp

I. INTRODUCTION

In a typical charge density wave (CDW) phase transition, the system first goes to an incommensurate (IC) state followed by an IC to commensurate (lock-in) transition as the temperature is lowered from the normal state above the CDW transition.[1–5] The CDW phase transition, signified by the presence of anomalies in various transport measurements, is further characterized by the appearance of superlattice reflection spots observable in electron or x-ray diffraction experiments. In real space, the IC phase is often characterized by the presence of discommensurations (DC's) or domain walls, and it is well known that nucleation, growth, and annihilation of DC's play the most critical role for the IC-commensurate transition.[6–9] As the temperature is lowered toward the commensurate phase, the density of DC continues to decline through motions and annihilations of DC's, leading to a gradual decrease in incommensurability of the superlattice diffraction spots. A few widely separated residual DC's strongly pinned by defects or impurities can sometimes still be seen in the commensurate phase. It should be noted that the CDW is an electronically homogeneous global phase transition and that the entire sample would undergo the transition as the critical temperature is approached.

In this paper, we report a new CDW state in the rare-earth transition-metal ternary silicide $Lu_2Ir_3Si_5$ by electron diffraction and direct observation in real space using a satellite dark-field imaging technique in transmission electron microscopy (TEM). Rare-earth transition-metal ternary silicides with three-dimensional crystallographic structures, such as the $R_5T_4Si_{10}$ and $R_2T_3Si_5$ types, have been shown to exhibit CDW phase transitions with remarkable anomalies observable in the thermal and electrical transport measurements.[10–14] The physical origin of the CDW formation in this class of materials is largely unknown due to a lack of detailed band structure calculations. However, it is believed that the intricate balance and competition of different electronic states could play a critical role and affect details of the CDW phase transition in this class of materials. A recent study of CDW in $Ho_5Ir_4Si_{10}$ showed that the CDW phase transition was accompanied by a concomitant cell-doubling crystallographic structural phase transition.[9] Previous reports also strongly suggested that the CDW in $Lu_2Ir_3Si_5$ was also accompanied by a similar structural phase transition.[15] In the present study of CDW in $Lu_2Ir_3Si_5$ we find a new electronically phase-separated CDW state in which CDW domains coexist with low-temperature normal phase domains. We find that, with a change in temperature, incommensurability remains unchanged in the present case, unlike other typical IC CDW systems in which incommensurability varies with temperature,[9] and the predominant change is in the redistribution of the area ratio of the two coexisting phases with the expansion of CDW domains at lower temperatures. We emphasize that the unprecedented phase-separated CDW state in $Lu_2Ir_3Si_5$ is an intrinsic electronic inhomogeneity, analogous to the electronic phase separation in manganites.[16–18] However, in manganites the concentrations for each phase are generally not determined by temperature, but rather by the charge-carrier concentrations. In the $Lu_2Ir_3Si_5$ CDW system, we find the transition is characterized by the accompanied changes of the spatial ratio of the two coexisting phases.

$Lu_2Ir_3Si_5$ adopts an orthorhombic structure ($U_2Co_3Si_5$, space group *Ibam*) at room temperature with lattice parameters that are determined to be $a = 9.914\ 57(5)$ Å, $b = 11.286\ 65(5)$ Å, $c = 5.721\ 91(5)$ Å.[15] Recent transport measurements[15,19] of $Lu_2Ir_3Si_5$ have shown a pronounced phase transition between 100 and 200 K, with a huge thermal hysteresis of 40 K. In this paper, we report the observation of incommensurate or nearly commensurate satellite reflections associated with the CDW phase transitions by electron diffraction and real-space imaging of CDW domains using a satellite dark-field imaging technique in TEM. We confirm the 40-K thermal hysteresis in our studies and the cell-doubling structural transition at low temperatures that competes with the CDW phase and gives rise to the new electronically phase-separated CDW state.

II. EXPERIMENTAL

The polycrystalline sample $Lu_2Ir_3Si_5$ was prepared by arc melting high-purity elements under an argon atmosphere. The sample has been remelted several times under the identical preparation conditions to improve the homogeneity and purity of phase. The resulting ingot was then sealed in a quartz ampoule with about 160 torr of argon and annealed at 1250 °C for 1 day followed by 14 days at 1050 °C. Transport measurements of this sample have been reported elsewhere.[19] Samples for the TEM studies were prepared by mechanical polishing followed by ion milling at liquid-nitrogen temperature. The thickness of our samples was estimated to be ∼70 nm using the bulk plasmon intensity in electron energy-loss spectroscopy. Our electron diffraction and TEM dark-field imaging[6,8,9] experiments were carried out using a JEOL 2000FX transmission electron microscope operating at 200 kV and equipped with a low-temperature sample holder capable of reaching 20 K and a 14-bit CCD imaging detector.

III. RESULTS AND DISCUSSION

TEM examination shows the typical grain size is larger than a few micrometers, which can be treated as single crystals in the present case since selected area electron diffraction patterns can be obtained from a much smaller area. Figure 1 compares [101] zone-axis electron diffraction patterns taken at room temperature and 95 K below the CDW phase transition. The room temperature diffraction pattern shown in Fig. 1(a) is consistent with the known orthorhombic lattice structure with space group *Ibam*. The presence of CDW superlattice spots can easily be seen in Figs. 1(b) and 1(c), and these superlattice spots are characterized by modulation wave vectors $\vec{q}_1 = \delta_1(\bar{1}21)$ and $\vec{q}_2 = \delta_2(12\bar{1})$, with δ_1 and δ_2, which are usually not the same, in the range of 0.23∼0.25. We note that Figs. 1(b) and 1(c) were obtained from different areas showing incommensurate CDW modulation in Fig. 1(b) and commensurate modulation in Fig. 1(c). The commensurability of CDW superlattice spots is found to vary from area to area, with most areas exhibiting incommensurate modulations. It is also noted that the incommensurate superlattice reflections are diffusive and elongated along the $(\bar{1}21)$ or $(12\bar{1})$ planar directions, indicating a rather short coherence length of ∼10 nm. The width of superlattice reflections in the orthogonal direction, however, is much narrower. Commensurate CDW superlattice spots, on the other hand, are much sharper in both directions. Electron diffraction patterns obtained from other zone axes such as [11-1] and [210] also yield the same CDW modulation wave vectors $\vec{q}_1 = \delta_1(\bar{1}21)$ and $\vec{q}_2 = \delta_2(12\bar{1})$. The appearance of CDW superlattice spots becomes discernible at ∼140 K upon cooling, and upon warming from low temperatures, they disappear at ∼180 K, with a 40-K thermal hysteresis, consistent with the recent transport measurement.[15,19] In addition to the CDW superlattice spots, forbidden Bragg reflections ($h0l$), which violate the extinction condition of $h, l = 2n$, such as (-101), (-303), and so forth, can also be seen in Figs. 1(b) and 1(c), signifying a structural phase transition associated with the CDW transition. This is consistent with previous x-ray diffraction results obtained at the liquid-nitrogen temperature showing a cell doubling along the c axis.[15] In our experiment, the structural phase transition temperature was found to be ∼15 K higher than the CDW superlattice formation for both cooling and warming, unlike the case in $Ho_5Ir_4Si_{10}$, where both CDW and structural phase transitions took place at the same temperature.[10–16] The higher structural transition temperature is also consistent with a recent thermal conductivity measurement which found that the anomaly from lattice contribution was ∼15 K higher than its electronic counterpart.[19]

TEM dark-field imaging using the CDW superlattice spots further reveals that the $\vec{q}_1 = \delta_1(\bar{1}21)$ and $\vec{q}_2 = \delta_2(12\bar{1})$ modulations as shown in Figs. 1(b) and 1(c) actually come from separate domains (but still in the same grain), which are marked as A and B, respectively, in Fig. 2. Note the big difference in DC density in these two domains, with domain A (thinner area) nearly commensurate, with few residual DC's, and domain B (thicker region) obviously incommensurate, with a very high density of DC's. Chemical microanalysis with an electron nanoprobe revealed no inhomogeneity between these two regions. The variations of local strains may have played an important role for the disparity of DC density in regions of different thicknesses. Crystallographically, $(\bar{1}21)$ and $(12\bar{1})$ reciprocal lattice vectors are equivalent and related by simple symmetry operations. This implies that the CDW phase transition is only characterized by one modulation wave vector, not two. The formation of a crystallographically equivalent CDW domain structure is a natural consequence

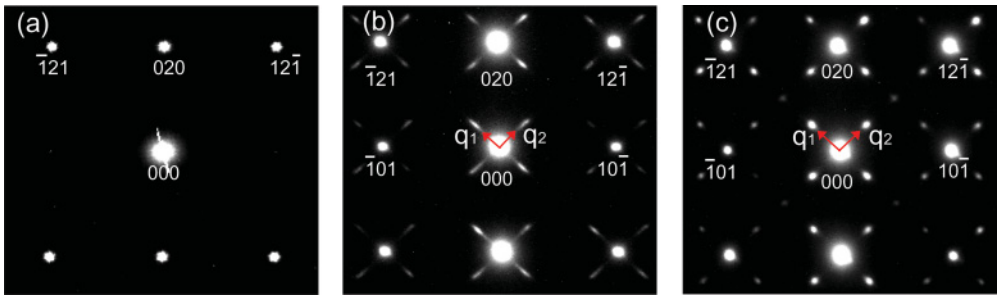

FIG. 1. (Color online) (a) The [101] zone-axis electron diffraction pattern obtained at room temperature. (b and c) Similar patterns obtained at 95 K that show the presence of CDW superlattice reflections and the systematic $(10\bar{1})$ reflections, which are absent at room temperature. CDW superlattice modulation in (b) is incommensurate, whereas (c) is obtained from a different area and is commensurate. We marked the modulation wave vectors $\vec{q}_1 = \delta_1(\bar{1}21)$ and $\vec{q}_2 = \delta_2(12\bar{1})$, with δ_1 and δ_2 varying ∼0.23–0.25 from area to area.

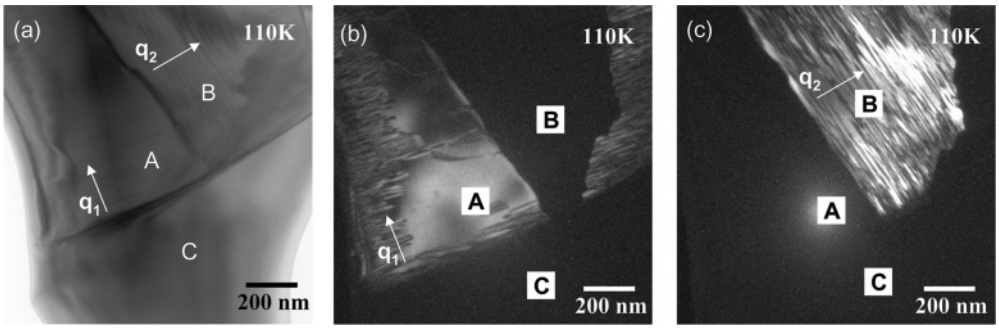

FIG. 2. (a) Bright-field image at 110 K of an area showing three domains marked as A, B, and C. (b and c) Dark-field images obtained from $\vec{q}_1$ and $\vec{q}_2$ superlattice spots, respectively. We note that modulation wave vectors $\vec{q}_1$ and $\vec{q}_2$ indicated in Fig. 1 actually come from different domains. It is noted that $\vec{q}_1$ is nearly commensurate and that $\vec{q}_2$ is incommensurate.

for a phase transition adopting a lower crystallographic symmetry at low temperatures. We note that the $\vec{q}_1$ and $\vec{q}_2$ domain structure shown in Fig. 2 can change during different thermal cycles in which areas originally characterized with $\vec{q}_1$ modulation can change into $\vec{q}_2$ modulation and vice versa. This indicates a weak pinning effect in $Lu_2Ir_3Si_5$. For most CDW systems, the modulation wave vector usually lies in a direction parallel to one of the principal high-symmetry axes; e.g., the modulation wave vector of CDW in a similar class of material, $Ho_5Ir_4Si_{10}$, is known to be along the c axis.[9] With the absence of band structure calculations in this class of materials, it is not completely clear why the modulation wave vector adopts an uncommon $(\bar{1}21)$ reciprocal lattice direction in the present case. Nevertheless, some clues can be gathered from the crystallographic structure of $Lu_2Ir_3Si_5$. It is noted that $2b^* \sim c^*$, and this makes the b and c components of the modulation wave vector nearly equal, probably enhancing the nesting geometry at the Fermi surface. The cell doubling along the c axis associated with structural phase transition shares the same physical considerations.

In the following, we will discuss the changes of the CDW superlattice spots and its domain structure as a function of temperature. Figure 3(a) shows an intensity profile of an incommensurate CDW superlattice reflection as a function of temperature. It is clear that the position and the width of the superlattice peak remain nearly unchanged in this temperature range, in striking contrast to typical incommensurate CDW systems, which normally exhibit gradual sharpening and movement toward the commensurate position of the superlattice peak as the temperature is lowered.[20,21] This very unusual observation set the CDW in $Lu_2Ir_3Si_5$ apart from the rest of known incommensurate CDW systems in which, as the temperature is lowered, the density of DC decreases through motions and annihilations of DC's, leading to a gradual decrease in incommensurability and the peak width of the superlattice diffraction spots.[6–9] The mystery of this anomalous CDW behavior in $Lu_2Ir_3Si_5$ is unveiled when we examine the CDW domain structure as a function of temperature in real space by the satellite dark-field imaging.

Close examination of the satellite dark-field images shown in Fig. 2 reveals that an electronic phase separation actually takes place during the CDW phase transition. In addition to the CDW domains A and B, domain C is present without CDW satellite modulations. Domain C represents the normal low-temperature phase, which is different from the high-temperature phase with the structural distortion mentioned earlier. In other words, the entire sample is phase separated into domains of CDW and regions without CDW. It should be noted that this phase coexistence appears within a single grain of the crystal. We have thoroughly studied many different

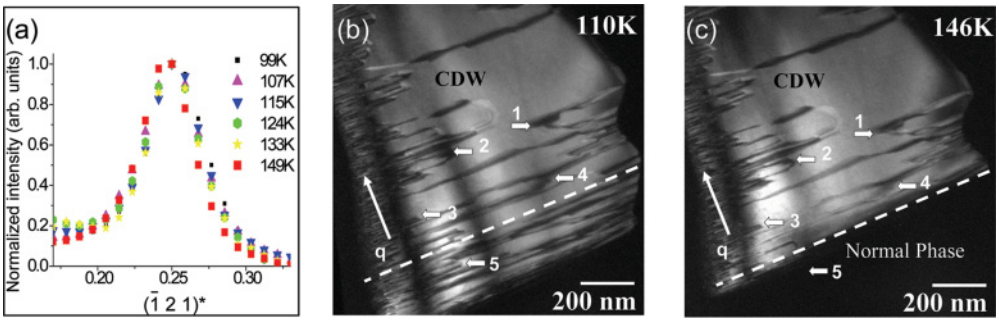

FIG. 3. (Color online) (a) Intensity profile of CDW superlattice reflections showing that the position and width remain largely unchanged as a function of temperature. (b and c) The CDW domain feature recorded at 110 and 146 K, respectively. With increasing temperature, the domain boundary (dashed line) separating the CDW phase (area with brighter contrast) and the low-temperature normal phase (area with dark contrast) moves in a direction along the CDW modulation wave vector such that the area of non-CDW phase grows at the expense of the CDW domain. It is noted that detailed configurations of discommensuration in the CDW domain, marked 1–5 for reference, remain unchanged with rising temperature.

samples, i.e., various grains in the same polycrystal and also from different polycrystals, and found this is a universal phenomenon. The spatial ratio of the CDW phase to the low-temperature normal phase is about 1:3 at 95 K. There exists a distinct, rather straight boundary between these two phases. As temperature varies, no changes of the density or detailed configuration of DC's within the CDW domains are observed. This is evidenced in Figs. 3(b) and 3(c), which display two dark-field images taken at 110 and 146 K, respectively. Several distinct features of DC's are labeled as 1 to 5 in both Figs. 3(b) and 3(c) for reference and comparison. It is clear that no discernible change or movement of DC's has taken place. The only change is the motion of the boundary separating the two phases, leading to an expansion of the CDW domain with decreasing temperature and vice versa. The motion of the boundary, which is thermally reversible, is indicated by the dashed line in Fig. 3(b) as temperature changes. The distribution of these two coexisting phases and their spatial ratio are therefore temperature dependent. This explains why the peak position and width of CDW superlattice reflections do not change with temperature as we have noticed in electron diffraction experiments. We have also cooled the sample down to 20 K, and it is found that the CDW phase has now become a predominant phase covering ~90% of the area. It should be recalled that the initial CDW transition occurs at a much higher transition temperature, ~140 K. The transition appears to be a very sluggish one.

We emphasize that the unprecedented phase-separated CDW state in $Lu_2Ir_3Si_5$ described above is an intrinsic electronic inhomogeneity, similar to the electronic phase separation in manganites,[16–18] in which the coexistence of charge-ordered insulating domains and ferromagnetic metallic domains is a common phenomenon.[22,23] The electronic phase separation in manganites, which arises from the intricate interplay of charge, spin, orbital, and lattice degrees of freedom, plays the most crucial role for the colossal magnetoresistance effect through the percolative transport in the phase-separated state.[22–26] However, the spatial ratio of these two phases in manganites below the transition temperature is largely determined by the hole-carrier concentration and is rather insensitive to temperature changes, unlike the case for $Lu_2Ir_3Si_5$. None of the previously known CDW systems exhibit the coexistence of domains with and without CDW. CDW has been known to be a homogeneous global phenomenon. It is not clear why the delicate balance and competition between the CDW phase and the low-temperature normal phase manifest so remarkably in $Lu_2Ir_3Si_5$. Throughout our experiments, we find that incommensurability tends to vary among different grains in the same polycrystal and the pattern of phase co-existence in the same grain can also vary among different thermal cycles. It is then plausible that minute variations of local strains play a critical role for the mixture of these two phases. Under this scenario, the low-temperature normal phase would be construed to be areas under higher strain, and the development of CDW modulations would naturally relieve some strain and eventually become the predominant phase at lower temperatures. It is then plausible that the system might be sensitive to external pressure. However, no measurements under applied pressure for the present system have been reported so far, and these experiments could be very helpful for understanding the CDW phase transition in $Lu_2Ir_3Si_5$.

IV. CONCLUSION

We have reported the presence of superlattice reflections associated with the CDW phase transition below ~140 K by electron diffraction in the rare-earth transition-metal silicide, $Lu_2Ir_3Si_5$. The CDW modulation wave vector is found to be $\vec{q} = \delta(\bar{1}21)$ with $\delta = 0.23 \sim 0.25$. A large thermal hysteresis of ~40 K is observed from the electron diffraction experiment, consistent with that reported from transport measurements.[15,19] The incommensurability and the width of the CDW superlattice reflections are found to be largely unchanged as the temperature varies. Dark-field images obtained from CDW superlattice reflections reveal unprecedented electronic phase separation in the CDW state consisting of a mixture of CDW domains and low-temperature normal phase domains without CDW. Changing the temperature causes only the motion of the boundary separating these two phases and therefore changes the ratio of their spatial extent, with the CDW phase prevailing at lower temperatures. Detailed configurations of DC are found to be intact and do not change with temperature, unlike typical CDW systems, in which motions, nucleations, and annihilations of DC's play the most critical role for the CDW phase transitions.[6–9]

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