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Commensurate charge-density wave with frustrated interchain coupling in $SmNiC_2$

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Temperature-dependent x-ray diffraction on $SmNiC_2$ has shown that the orthorhombic lattice symmetry of this compound persist down to a temperature of at least 9 K, i.e., into the charge-density-wave (CDW) state below $T_{CDW}=148$ K and in the ferromagnetically ordered state below $T_C=17.7$ K. The modulated crystal structure has been determined for the incommensurate CDW state with $\mathbf{q}_{CDW}=(0.5,0.516,0)$ at $T=60$ K. The observed atomic modulation displacements indicate that the CDW should be considered as a commensurate CDW centered on chains of Ni atoms along **a**. Frustrated interchain coupling is responsible for the incommensurability of the three-dimensionally ordered CDW state.

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I. INTRODUCTION

Ternary carbides RTC_2 containing a rare-earth (R) and a transition-metal (T) element have been synthesized in 1980s for the complete series of rare-earth elements and several transition metals, such as Mn, Fe, and Ni.[1–3] The rare-earth elements are responsible for the paramagnetic properties and the development of antiferromagnetic (AF) order at low temperatures in most compounds $RNiC_2$.[4,5] Exceptions are $LaNiC_2$, which is nonmagnetic and develops superconductivity with $T_C=2.7$ K,[6] and $SmNiC_2$, which becomes ferromagnetic (FM) below $T_C=17.7$ K.[5]

The phase diagram of $SmNiC_2$ is complicated by the appearance of a charge-density wave (CDW) below $T_{CDW}=148$ K.[7] Satellite reflections have been found in x-ray diffraction below T_{CDW} at incommensurate positions given by the modulation wave vector $\mathbf{q}_{CDW}=(0.5,\sigma_2,0)$ with $\sigma_2=0.516$ at $T=60$ K.[8] The CDW disappears at T_C where FM order develops.

Compounds $RNiC_2$ and $R_5Ir_4Si_{10}$—both containing rare-earth elements—are of interest because they are atypical, strong-coupling CDW systems and provide the opportunity to study the interplay between CDWs and magnetism.[8,9] Like $SmNiC_2$, $Er_5Ir_4Si_{10}$ has an incommensurate CDW below 155 K but it develops AF order below $T_N=2.8$ K.[10] $Lu_5Ir_4Si_{10}$ has a commensurate CDW below 83 K;[9] it is nonmagnetic and develops superconductivity below 3.9 K.[11] Unlike $SmNiC_2$, the CDWs persist in the AF and superconducting phases of these compounds.[9,12]

Similarities between the CDWs in $SmNiC_2$ and $Er_5Ir_4Si_{10}$ include anomalies at the respective transition temperatures in the temperature dependencies of the electrical resistivity, the lattice parameters, and the specific heat.[7,8,10] The temperature dependencies of the magnetic susceptibility exhibit clear anomalies at T_C or T_N but the CDW transitions are invisible in these experiments.[5,10] This has been explained by the large contribution of local moments to the susceptibility as opposed to the contributions of Pauli paramagnetism.[8,10]

Canonical CDW compounds are characterized by a large anisotropy of their electrical resistivity, with the direction of the lowest resistivity defining the direction of the CDW.[13] A strong interchain coupling is responsible for a much lower anisotropy for $RNiC_2$ and $R_5Ir_4Si_{10}$ than found in canonical CDW systems, with values of $\rho_c/\rho_a\approx 5.0$ and $\rho_b/\rho_a\approx 2.8$ for $SmNiC_2$,[8] and of $\rho_a/\rho_c=\rho_b/\rho_c\approx 2.4$ for $Er_5Ir_4Si_{10}$.[10] However, an important difference exists between these compounds. In $Er_5Ir_4Si_{10}$, the **c** axis is the direction of both the smallest resistivity and the incommensurate CDW with $\mathbf{q}=(0,0,\sim 0.22)$. For $SmNiC_2$, the incommensurate component of $\mathbf{q}_{CDW}$ is along $\mathbf{b}^*$, suggesting an incommensurate CDW along **b** while the lowest resistivity is along **a**, suggesting the **a** axis as direction of the CDW. Electronic band-structure calculations of $SmNiC_2$ have indicated a CDW wave vector of (0.5, 0.56, 0), close to the observed $\mathbf{q}_{CDW}$.[14] However, the published Fermi surface is composed of warped planes perpendicular to **a**,[14] a feature which would support the interpretation of **a** as the direction of the CDW, in agreement with the classical picture of band structures of CDW materials.[13]

Here we will show that the CDW in $SmNiC_2$ should be interpreted as a commensurate CDW centered on chains of Ni atoms along **a**. The observed pairing of Ni atoms is intrinsically frustrated on the lattice of $SmNiC_2$, and this frustration is proposed to be responsible for the incommensurate component of $\sigma_2\approx 0.516$ of $\mathbf{q}_{CDW}$.

II. EXPERIMENTAL

Single-crystalline material of $SmNiC_2$ has been used as described before.[8] A crystal of dimensions $0.12\times 0.06\times 0.035$ mm^3 was selected for x-ray diffraction experiments using synchrotron radiation of wavelength 0.5600 Å. The crystal was glued to a carbon fiber that was attached to the cold finger of a closed-cycle helium cryostat mounted on the Huber four-circle diffractometer at beamline D3 of Hasylab at DESY, Hamburg, Germany. X-ray diffraction was measured with a scintillation detector at selected temperatures between 9 K and room temperature. Preliminary x-ray diffraction experiments have been performed on a Nonius MACH3 diffractometer with Mo $K\alpha$ radiation from a rotating anode generator. They confirmed the orthorhombic $CeNiC_2$ structure type with space group $Amm2$ and lattice

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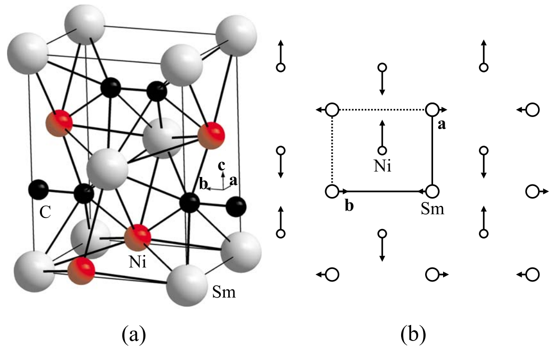

FIG. 1. (Color online) (a) Crystal structure of $\mathrm{SmNiC_2}$. (b) One layer of Sm/Ni atoms with atomic displacements (multiplied by 25) due to the modulation indicated by arrows for $t=0.246$.

parameters $a=3.7037(3)$, $b=4.5279(2)$, and $c=6.0947(4)$ Å at room temperature, in agreement with previous studies [Fig. 1(a)].[1,3] The crystal shape was determined by refinement against ψ scans of selected reflections, and it was subsequently used for absorption correction of the intensity data (see below).

The synchrotron experiment was used to determine the orthorhombic lattice parameters at low temperatures. At $T=60$ K, they are $a=3.6965(5)$, $b=4.5293(7)$, and $c=6.0955(8)$ Å. In a first experiment, so-called ω-2θ maps were measured for the three reflections $(02\bar{2})$, $(20\bar{4})$, and $(2\bar{2}0)$. For this purpose, the detector slits were set to 6×0.02 mm^2, corresponding to an acceptance angle in the direction of 2θ of 0.0031°. Centered on each reflection ω scans of 101 steps were carried out for a series of 81 2θ values with step sizes of 0.003° in ω and 0.002° in 2θ. The results give the diffracted intensity as a function of the orientation of the crystal and the scattering angle. For the orthorhombic lattice, all reflections are expected to appear as single peaks. A splitting of one of the three reflections $(02\bar{2})$, $(20\bar{4})$, and $(2\bar{2}0)$ would indicate a monoclinic lattice distortion, with monoclinic angle α, β, or γ, respectively. At 60 and 9 K, all ω-2θ maps exhibit single maxima (Fig. 2). These results show that the lattice remains orthorhombic in both the CDW and the FM-ordered phases.

Within the CDW phase, q scans along $\mathbf{b}^*$ and centered on $(0.5\ 3\ \bar{2})$ confirmed the presence of satellite reflections with modulation wave vector $\mathbf{q}_{\mathrm{CDW}}$ and $\sigma_2=0.516$ at a temperature of 60 K. Employing this modulation wave vector, intensities were measured by ω scans of the Bragg reflections $(hklm)$ up to $\sin(\theta)/\lambda=0.74$ Å^{-1}. All main reflections ($m=0$) and first-order satellites ($|m|=1$) were measured. ω scans at the positions of 71 second-order satellites ($|m|=2$) up to $\sin(\theta)/\lambda=0.41$ Å^{-1} and of 84 second-order satellites for $0.57<\sin(\theta)/\lambda<0.74$ Å^{-1} showed that they were too weak to be measured in our experiment. Integrated intensities were corrected for Lorentz and polarization effects and for absorption. Averaging in point symmetry $mm2$ resulted in a data set of 119 main reflections and 192 first-order satellite reflections, of which 119, respectively, 185 reflections had intensities larger than three times their standard uncertainties (observed reflections).

The modulated crystal structure has been described within the superspace approach, with a symmetry given by the superspace group $Amm2(\frac{1}{2}\sigma_2 0)000$.[15,16] The intensities of the first-order satellite reflections could be described by a displacive modulation consisting of single-harmonic functions for all three crystallographically independent atoms in the unit cell of the average structure,

$$u_i(\bar{x}_{s4}) = A_i \sin(\bar{x}_{s4}) + B_i \cos(\bar{x}_{s4}) \tag{1}$$

for $i=x,y,z$ and with $\bar{x}_{s4}=t+\mathbf{q}_{\mathrm{CDW}}\cdot\mathbf{x}^0$, where t is the phase of the modulation wave and $\mathbf{x}^0$ are the basic-structure coordinates. Structure refinements with the computer program JANA2006 (Ref. 17) resulted in an excellent fit to the diffraction data with $R_F=0.014$ for the main reflections and $R_F=0.031$ for the satellites (Table I).

III. DISCUSSION

The crystal structure [Fig. 1(a)] does not allow a straightforward identification of the atomic chains carrying the

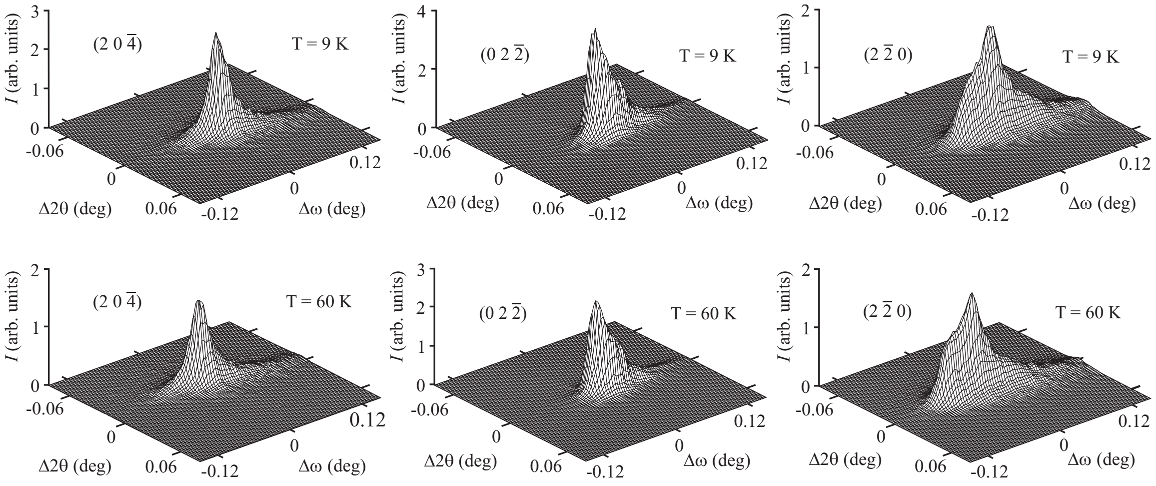

FIG. 2. Diffracted intensity (I) as a function of scattering angle 2θ and crystal orientation ω for three reflections at the temperatures of 60 and 9 K. $\Delta 2\theta$ and $\Delta\omega$ indicate the deviations from the center of the scans. The intensity is in arbitrary units.

TABLE I. Structural parameters at $T=60$ K. (x^0, y^0, z^0) are the fractional coordinates of the basic structure; modulation amplitudes according to Eq. (1) are given in angstrom; and the equivalent isotropic atomic displacement parameter is given in square angstrom. Standard uncertainties are in parentheses. $B_y=A_z=0$ for all atoms.

Atom	x^0	y^0	z^0	A_x (Å)	B_x (Å)	A_y (Å)	B_z (Å)	U_{iso}^{eq} (Å^2)
Sm	0	0	0	0	0	0.0270(2)	0.0116(1)	0.0022(1)
Ni	0.5	0.5	0.1115(2)	−0.0501(5)	0	0	0	0.0032(3)
C	0.5	0.1519(21)	0.2948(16)	−0.0001(20)	0.0200(23)	0	0	0.0066(20)

quasi-one-dimensional (1D) valence band responsible for the CDW since all atoms could contribute to it. In the basic structure at 60 K, shortest Ni-Ni and Sm-Sm distances are equal to the lattice parameter $a=3.697$ Å, and chains along **a** of either type of atom would qualify as 1D system. The shortest distances between metal atoms are, however, between Ni and Sm with values of 3.001(0) and 3.004(1) Å while distances between atoms apart by the centering translation are equal to 3.797(2) Å and only slightly larger than the shortest distance between atoms of the same kind. Therefore, the low-dimensional electron band could be a mixed Sm/Ni band on layers perpendicular to **c** or pure Sm or pure Ni bands on layers perpendicular to **a**. Simple atomic chains along **b** are unlikely because of the long distance of $b=4.529$ Å between those atoms. The identification of the 1D system within the basic structure depends on the orbital contributions to the valence band and can only be obtained through electronic band-structure calculations.

A periodic lattice distortion is intrinsic to CDWs because the gain of electronic energy is achieved through a modulation of the positions of the atoms carrying the low-dimensional valence band responsible for the CDW. Ni atoms exhibit the largest modulation amplitude (Table I), and they should, therefore, carry the CDW. This interpretation is supported by the variation in interatomic bonding distances due to the modulation wave, which is by far the largest variation for the Ni atoms neighboring along **a** (Fig. 3). The modulations of Sm and C follow those of Ni, such that the shortest interatomic distances remain as constant as possible (Fig. 3).

The crystal structure can be described as a stacking along **c** of layers of Sm and Ni atoms, i.e., the layer at $z=0$ contains Sm atoms at $z=0$ and Ni atoms at $z=0.1156$ [Fig. 1(a)]. Carbon atoms are located between the layers. In Fig. 1(b), the structure of one layer is given together with arrows indicating the atomic displacements due to the modulation wave for a phase of $t \approx 0.25$. The Ni atoms form dimerized chains along **a**, suggesting this to be the direction of the CDW. Neighboring chains are out of phase, as it is imposed by elastic coupling via Ni-Sm-Ni bond paths. Only an antiphase relation between neighboring chains allows displacements of Sm atoms leading to the minimization of the variation in the shortest metal-metal bonds within the layers. The optimal modulation wave vector would be (0.5, 0.5, 0) for single layers.

Neighboring layers are related by the *A* center. Their phase difference would be 90° for a commensurate CDW with wave vector (0.5, 0.5, 0). Atoms, which are modulated

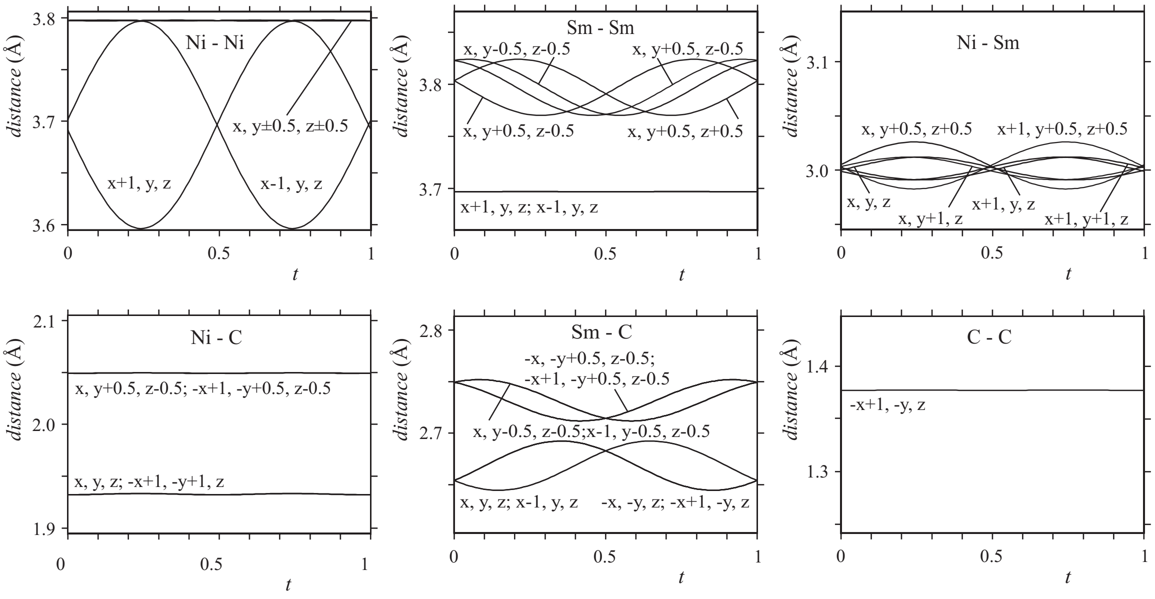

FIG. 3. Interatomic distances as a function of the phase *t* of the modulation wave. Symmetry operators apply to the second atom in each pair. Atomic coordinates from Table I.

in one layer would have zero displacements in the neighboring layers. The resulting structure—although not impossible—appears unlikely because all Ni atoms have identical environments and only half of them would participate in the CDW. On the other hand, unequal modulations of Ni atoms would imply the loss of the A center, in which case symmetry would not enforce a relation between the modulations of Ni atoms on neighboring layers. The A center appears to provide a perfect frustration between the modulations on chains of nickel atoms in neighboring layers, which can only be resolved by zero modulation amplitude on every second layer, or by an incommensurate coupling between the layers—as it is the observed experimentally. This explains the incommensurability of the second component, $\sigma_2 = 0.516$, of $\mathbf{q}_{\mathrm{CDW}}$.

Carbon is present in the structure as C_2 units with a C-C distance of 1.376(13) Å, almost equal to a typical value for a C-C double bond. This distance does not vary in the modulated structure, indicating that carbon does not participate in the CDW because any variation in the charge-transfer between carbon and the metal atoms would have modified the character, and therefore the length of the C-C bond.

The electronic band structure of $SmNiC_2$—calculated within the local-density approximation—has lead to the identification of a maximum in the electronic susceptibility at a wave vector of (0.5, 0.56, 0) close to the observed incommensurate modulation wave vector of the CDW.[14] The nesting condition is, however, between parts of the Fermi surface that are warped planes perpendicular to the direction of **a**, and separated by the commensurate value of $\sigma_1 = 0.5$. The other nonzero component of $\mathbf{q}_{\mathrm{CDW}}$ is parallel to the Fermi surface and it is explained by the warped character of these planes in a way similar to that for canonical CDW systems such as $NbSe_3$.[18] In those cases, the parallel component has always been commensurate while in the present case, it has been found to be incommensurate.

We have demonstrated here that there is frustration between the CDW modulations on neighboring atomic planes perpendicular to **c**, and we propose that this frustration is responsible for the incommensurability of second component of the CDW wave vector. The frustration pertains to the periodic lattice distortion intrinsic to the CDW but it is also reflected in the electronic band structure, thus explaining the incommensurability of the nesting vector found in Ref. 14.

Important evidence for the direction of the CDW comes from fluctuations above T_{CDW}, as they can be observed by diffuse x-ray scattering. Shimomura *et al.*[8] have reported the temperature dependence of the diffuse scattering in the $\mathbf{b}^*, \mathbf{c}^*$ plane, i.e., concentrating on the direction given by the incommensurate component of $\mathbf{q}_{\mathrm{CDW}}$. A reanalysis of those data, now including the diffuse scattering at $T = 160$ K in the $\mathbf{a}^*, \mathbf{b}^*$ plane, shows that the correlation lengths at this temperature are 116 Å along **a** and 94 Å along **b**. The longer correlation length along **a** supports the notion that **a** rather than **b** is the direction of the CDW. It would be interesting to obtain these correlation lengths as a function of temperature up to at least room temperature. The proposed direction of the CDW chains along **b** would require a slower decrease in the correlation length along **b** than along **a**. Such experiments would require a considerable amount of beam time at a synchrotron source, and they are beyond the scope of the present work.

IV. CONCLUSIONS

We have shown that the lattice of $SmNiC_2$ remains orthorhombic within the CDW and ferromagnetic phases. The incommensurately modulated structure provides compelling evidence for a CDW that is centered on the chains of Ni atoms along **a**. The observed CDW should be interpreted as a commensurate CDW (twofold superstructure) centered on the chains of Ni atoms along **a**, which then have a frustrated three-dimensional coupling, leading to the observed incommensurability of the modulated structure of the CDW state. Of course, the present analysis does not exclude possible contributions of Sm orbitals to the low-dimensional valence band.

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