Density, excess volume, and structure of Fe–Cr–Ni melts

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ABSTRACT

The relationship between the excess volume and the structure of Fe–Cr–Ni melts is investigated using containerless levitation and *in situ* high-energy synchrotron x-ray diffraction techniques. The density of six hypoeutectic Fe–Cr–Ni alloys along the 72 wt. % Fe isopleth was measured in the stable and undercooled regions, and the excess volume was evaluated as a function of Cr concentration. It is found that the 72Fe–Cr–Ni alloys exhibit a positive sign of excess volume and the amount increases with increasing Cr concentration. Analysis of the structure factor and pair distribution function of the alloy family reveals that the short-range order in the melt becomes more pronounced with decreasing Cr concentration; this demonstrates a direct correlation between the excess volume and local liquid structure. A characteristic signature of the icosahedral structure is observed in the structure factor of the melts, and the potential origin of the positive excess volume of the 72Fe–Cr–Ni alloys is qualitatively discussed in relation to the icosahedral structure.

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I. INTRODUCTION

Understanding the solution behavior of alloys of two or more constituents requires the quantification of excess values defined as the difference between experimental and ideal values for the thermophysical properties.^{1,2} The excess value was often correlated with anomalies in the structure,^{3,4} thermodynamic,^{5–7} and kinetic properties^{8,9} of glass and quasicrystal forming alloys, revealing the origin of alloy formation. In this view, excess volume has attracted much attention since it gives a macroscopic perspective on how atoms interact with each other in the melt and the interaction is seen to vary with temperature and composition. The excess volume has also been recognized as a key parameter in understanding the stability and crystallization pathways for undercooled melts.^{7,10}

It has been widely accepted that there is a rough dependence between the atomic interaction and excess volume in metallic melts;¹¹ immiscible systems tend to exhibit a positive sign of excess volume, strongly mixing systems show a negative excess volume, and configurations of elements with similar chemical properties show an excess volume of almost zero. Excess thermodynamic properties (i.e., excess Gibbs free energy, excess entropy, and heat of mixing)

have been considered as a predictor for the behavior of atomic interactions, but many exceptions have been reported that contradict this trend.^{12–15} Watanabe *et al.*¹² argued that the excess volume of binary alloy melts is closely correlated with the excess Gibbs free energy, rather than the excess entropy and heat of mixing. It was also reported that the atomic size ratio between constituents also significantly affects the atomic packing efficiency and thus the excess volume.¹⁰ Due to such a complex combination of chemical and topological factors on atomic interactions, predicting and understanding the sign of excess volume is still challenging. Furthermore, the direct correlation between the excess volume and the structure in melts has been rarely reported to date.

The Fe–Cr–Ni system is one of the alloy systems representing the exceptional case; Fe, Cr, and Ni elements belong to the same period on the periodic table and have similar atomic radii. Their binary and ternary combinations on composition show a negative heat of mixing and excess Gibbs free energy, but they have been reported to exhibit a positive excess volume.^{12,16,17} This system is also of significant practical importance since Fe–Cr–Ni based steels (72Fe–Cr–Ni) with an iron content of around 72 wt. % present the basis for the technically important stainless

steel classification including the SS300 series alloys 304, 316, and 347. Proper values of the density or molar volume and thermal expansion of Fe–Cr–Ni based steels are needed for correct modeling of the solidification and phase transformation behavior during casting and welding manufacturing operations. So far, the simulations have been based on the ideal mixing approximation (no excess volume).^{18,19}

In this work, we report the experimental results for density, excess volume, and structure of 72Fe–Cr–Ni alloy melts. Six compositions were selected with Cr concentrations of 7 wt. %, 9 wt. %, 11 wt. %, 12 wt. %, 14 wt. %, and 16 wt. % by considering the practical composition range of technically important stainless steels. The density measurements were carried out using the electrostatic levitation (ESL) technique. *In situ* synchrotron x-ray diffraction (XRD) experiments were carried out to further study the Cr dependence on the excess volume and the relation between the excess volume and the structure of the 72Fe–Cr–Ni melts.

II. EXPERIMENTAL

A. Electrostatic levitation

Fe–Cr–Ni alloys were prepared by arc-melting the pure elements (Fe 99.95%, Ni 99.999%/Alfa Aesar, Cr 99.999%/ESPI) under an Ar atmosphere. A zirconium sphere was used as an oxygen getter to scavenge the remaining oxygen in the arc-melting chamber prior to melting of the constituents. The mass loss during alloying in the arc-melting process was less than 0.2% of the initial mass. In this work, the compositions of 72Fe–Cr–Ni are given in wt. % (refer to Table SI in the [supplementary material](#) for the compositions in at. %).

The ESL facility at the NASA Marshall Space Flight Center (MSFC) in Huntsville AL was used for the density measurements. Samples with a mass of ~35 mg (a diameter of ~2 mm) were levitated between two electrodes and melted by using a high voltage amplifier and a Nd-YAG high power laser under ultrahigh vacuum (UHV) conditions of 10^{-7} Torr. The temperature of the levitated sample was monitored with a LumaSense Technologies IMPAC IGA 140 single-color pyrometer, which is operated at a wavelength range of 1.45–1.8 μm . For density evaluation of the alloys, an UV imaging technique^{20,21} was used to capture the laser back-lit shadow of levitated samples using a high-speed camera operated at an acquisition rate of 30 fps. The camera was focused such that radial color gradient across the edge of the projected sample image was between 4 and 8 pixels. A tungsten-carbide sphere with a diameter of 2.2 mm was used for the calibration to establish the required pixel-to-meter conversion factor. During the analysis of digital images, the midpoint of color gradient across the edge of the sample was found and the encompassed area was taken to be the projected area of the sample assuming vertical axisymmetric symmetry.²² From the obtained sample volumes, the melt density was calculated.

B. *In situ* x-ray diffraction

In situ synchrotron XRD experiments were conducted at the P07 high-energy material science beamline of the third-generation radiation source PETRA III at the Deutsches Elektronen-Synchrotron (DESY) in Hamburg²³ using an electromagnetic levitation (EML) facility developed by IFW Dresden. Samples with a

mass of ~1.1 g (a diameter of ~6 mm) were placed in an UHV chamber backfilled to 450 mbar with high purity He gas after evacuation. Positioning and heating of the sample under investigation were realized with a water-cooled copper coil powered by a 10 kW generator operating at 280 kHz. Active sample cooling was achieved by recirculation of the inert gas (He) around the sample surface. The temperature of the levitated sample was monitored with a Mer-genthaler single-color pyrometer operated at a wavelength range of 1.6–2.1 μm . High-energy ($E = 98$ keV, $\lambda = 0.1264$ Å) diffraction measurements were conducted in transmission mode using a hybrid pixel PILATUS3 X 2M CdTe detector (DECTRIS) at a sampling rate of 250 Hz. The recorded two-dimensional diffraction patterns were azimuthally integrated using the FIT2D software.^{24,25} The total structure factor $S(q)$ and pair distribution function (PDF) $g(r)$ were derived from the measured diffraction data after corrections for background, absorption, multiple scattering, fluorescence, and Compton scattering using the PDFgetX2 software.²⁶ During data analysis, neither a data smoothing routine nor a damping procedure was applied when conducting the Fourier transformation from $S(q)$ to $g(r)$.

III. RESULTS

A. Density and thermal expansion

The six 72Fe–Cr–Ni alloys were heated up to their respective liquidus temperatures T_L to disperse, evaporate, or dissolve any oxygen-containing phases on the surface of the melts. Since heterogeneous nucleation sites are minimized by using containerless processing techniques, the melts could be undercooled significantly below the T_L when the heating laser is turned off. Upon cooling, the volume of the melts was obtained as a function of temperature. In the ESL experiments, thermal processing of each individual sample was limited to three melt cycles to minimize the compositional change of samples due to evaporation at elevated temperatures. The potential for composition changes during testing is attributed to differences in the vapor pressure of Fe, Cr, and Ni elements at temperatures significantly above T_L . Characterizing the evaporation and differential mass loss is done in the manner described in the previous work.^{22,27} Using these methods, the compositional shift is predicted to be less than 1% for each constituent and the standard uncertainty is estimated to be less than 2%.

The mean values of the density for the 72Fe–Cr–Ni melts studied are shown in [Fig. 1](#). They were obtained by averaging over the three measured datasets for each composition, presented in [Fig. S1](#) in the [supplementary material](#). In general, most alloys exhibit a constant thermal expansion with temperature, and thus, the density increases linearly with decreasing temperature. Previously, a weakly non-linear relation between the density and temperature was observed for liquid Si²⁸ and NiTi melt.²⁹ The present results for the 72Fe–Cr–Ni melts show that the density increases linearly with decreasing temperature in the stable and undercooled regions. The temperature dependence is expressed by a linear law over the entire range of Cr concentration and temperature investigated,

$$\rho = \rho_L + A(T - T_L), \quad (1)$$

where ρ_L is the density at T_L and A is the temperature coefficient ($\Delta\rho/\Delta T$). The parameters of the linear fits are given in [Table I](#). The

FIG. 1. (a) Density ρ of the 72Fe–Cr–Ni melts with Cr concentration as a function of temperature T . Solid lines are linear fits of the density values for each composition. Density of the 72Fe–Cr–Ni melts as a function of Cr concentration at (b) their respective T_L and (c) at 1750 K. Error bars indicate the standard deviation; they are not shown in panel (a) for the clarity of presentation.

ρ_L of the 72Fe–Cr–Ni alloys is shown as a function of Cr concentration in Fig. 1(b) and is compared to density values at a constant temperature of 1750 K in Fig. 1(c). Both density values are almost identical at each composition due to a small difference between their respective liquidus T_L and 1750 K and show an approximate linear decrease with increasing Cr concentration. Previous studies using EML¹⁷ and modified pycnometric³⁰ techniques reported that the

density of Cr–Ni melts decreases with increasing Cr concentration. In combination, these observations imply that the density of liquid Ni is higher than that of liquid Cr at 1750 K. It is also supported with the fact that the molar mass (58.693 g mol⁻¹) of Ni is higher than that (51.996 g mol⁻¹) of Cr. Alternatively, the density of liquid Fe–9.29Cr–18.87Ni (wt. %) was reported to be 7.09 g cm⁻³ at 1748 K,¹⁶ and this value is in agreement with that of Fe–9Cr–19Ni within 0.42%

Figure 2 shows the thermal expansion coefficient α_V ($= V^{-1} dV/dT$, V = sample volume) of the 72Fe–Cr–Ni melts as a function of Cr concentration at 1750 K, which was calculated from the measured volume–temperature data. In the previous work, a characteristic relation between density and thermal expansion coefficient was reported for binary metallic melts; both show a linear or a non-linear trend with solute concentration.¹⁰ For the 72Fe–Cr–Ni melts, the thermal expansion coefficient shows an approximate linear increase with Cr concentration, but no clear relation between the thermal expansion coefficient and density is observed due to the narrow composition range and the large error of experimental results. The thermal expansion coefficient of Fe–9Cr–19Ni is in agreement with that of Fe–9.29Cr–18.87Ni within 5.5%.¹⁶

B. Excess volume

The density change with Cr concentration is further discussed with excess volume defined as the difference between experimental and ideal volumes as follows:

$$V_m = \sum_{i=1}^n c_i \frac{M_i}{\rho_i} + \Delta V_m, \quad (2)$$

where V_m is the experimental molar volume, ΔV_m is the excess volume, and ρ_i , c_i , and M_i are the density, mole fraction, and molar volume of constituents, respectively. The summation term represents the calculated molar volume, which for an ideal system is defined by Vegard's law.^{1,2} In order to investigate the excess volume of the 72Fe–Cr–Ni alloys, we first measured the density of Fe and Ni using the same ESL techniques as employed for the Fe–Cr–Ni alloys. The measured density and temperature coefficients for pure Fe and Ni are also given in Table I. The ρ_L of Fe and Ni is determined to be 6.968 g cm⁻³ and 7.929 g cm⁻³, respectively. Compared to the previous results, these values are in good agreement to within $\pm 0.31\%$ and $\pm 0.68\%$ for Fe^{17,22,31} and Ni,^{12,32,33} respectively, and reasonable deviations within $\pm 1.07\%$ and $\pm 1.75\%$ are also found for

TABLE I. Experimental results for density ρ and temperature coefficient A of the 72Fe–Cr–Ni alloys, Fe, and Ni at their respective T_L and 1750 K.

Cr (wt. %)	T_L (K)	ρ_L (g cm ⁻³)	$-A$ (10 ⁻⁴ g cm ⁻³ K ⁻¹)	ρ at 1750 K	T Range (K)
7	1747	7.088 ± 0.007	6.208 ± 0.036	7.087 ± 0.007	1601–1839
9	1746	7.062 ± 0.005	6.189 ± 0.059	7.060 ± 0.006	1613–1846
11	1744	7.026 ± 0.008	6.826 ± 0.069	7.021 ± 0.007	1662–1840
12	1743	7.018 ± 0.022	6.557 ± 0.065	7.013 ± 0.020	1655–1849
14	1740	6.979 ± 0.005	6.890 ± 0.093	6.973 ± 0.016	1667–1842
16	1735	6.944 ± 0.015	6.450 ± 0.047	6.934 ± 0.010	1651–1842
Pure Fe	1811	6.968 ± 0.033	7.113 ± 0.057	7.011 ± 0.047	1693–1900
Pure Ni	1728	7.929 ± 0.041	7.828 ± 0.065	7.912 ± 0.034	1631–1824

FIG. 2. Thermal expansion coefficient α_v of the 72Fe–Cr–Ni melts as a function of Cr concentration at 1750 K. The thermal expansion coefficient was determined by linear fitting of the measured volume-temperature data. Errors indicate the standard deviation.

FIG. 3. (a) Molar volume V_m and (b) excess volume ΔV_m of the 72Fe–Cr–Ni melts as a function of Cr concentration at 1750 K. The results corresponding to the different values of Cr density are marked by squares³⁵ and circles,³⁶ respectively. Error bars indicate the standard deviation.

Fe¹² and Ni,³⁴ respectively. Due to the extremely high evaporation of Cr at high temperatures, the density of liquid Cr was taken from two literature data, showing the temperature dependence of $7.87 - 0.00091 \times T$ (in centigrade)³⁵ and $6.29 - 0.0011 \times (T - T_L)$,³⁶ respectively, and from the equations, the density of liquid Cr is determined to be 6.527 g cm^{-3} and 6.763 g cm^{-3} at 1750 K, respectively.

Figure 3 shows the molar volume V_m and excess volume ΔV_m of the 72Fe–Cr–Ni melts as a function Cr concentration at 1750 K. The results calculated from the different values of Cr density are marked by circles³⁵ and squares,³⁶ respectively. In the Cr concentration range investigated, the excess volume exhibits a positive sign and the amount increases with increasing Cr concentration. Although there are no reported results for excess volume of the 72Fe–Cr–Ni compositions, Kobatake and Brillo¹⁶ showed that the excess volume of Fe–10Cr–Ni ($18 \leq \text{Fe} \leq 72$, at. %), Fe–20Cr–Ni ($16 \leq \text{Fe} \leq 64$, at. %), and Fe–40Cr–Ni ($12 \leq \text{Fe} \leq 48$, at. %) melts exhibits a positive sign. The positive excess volume was also found in the Fe–Ni and Fe–Cr melts showing a maximum value of about $0.1 \text{ cm}^3 \text{ mol}^{-1}$ at 1773 K¹⁷ and this value is close to that on the excess volume of the 72Fe–Cr–Ni alloys presented in Fig. 3(b).

IV. DISCUSSION

Wang *et al.*³⁷ showed a relation between the excess volume and the liquid structure of binary La-based liquids using ESL and *in situ* synchrotron XRD techniques, arguing that the positive excess volume of La–Cu liquid could be a result of a steep repulsion and anharmonic attraction of the potential. An analysis of the excess volume and undercoolability of Zr–Ti and Zr–Hf liquids revealed that effective atomic packing close to ideal icosahedral dense packing can affect the degree of ISRO and its stability in liquids.¹⁰ These results mean that in metallic melts, the excess volume reflects a character of short-range order (SRO), which is determined by a combination of interatomic interactions and geometrical factors.^{38,39} Based on structural analysis of the neutron diffraction data, Cuello *et al.*⁴⁰ also showed that the coordination number (CN) of Fe₉₀Ni₁₀ liquid is higher than that of Fe₈₅Ni₁₅, which is consistent with the behavior of excess volume in liquid Fe–Ni alloys.

In view of the above-mentioned results, we analyze the behavior of excess volume of the 72Fe–Cr–Ni alloys from a structural point of view. By assuming an ideal hard sphere (HS) mixture for the 72Fe–Cr–Ni system, one can estimate the effective HS packing fraction ϕ to quantify the amount of the positive excess volume, which is defined as $\phi = \pi \rho_0 d^3/6$, where d is the averaged atomic diameter and ρ_0 is the number density given by $\rho_0 = \rho N_a/M_0$, where ρ is the density, N_a is the Avogadro number, and M_0 is the averaged molar mass, respectively. The number density of the 72Fe–Cr–Ni alloys at 1750 K, calculated from the measured mass density, is shown in Fig. S2 in the [supplementary material](#). With the covalent radii of Fe, Cr, and Ni proposed by Pauling,⁴¹ $d_{\text{Fe}} = 2.33 \text{ \AA}$, $d_{\text{Cr}} = 2.34 \text{ \AA}$, and $d_{\text{Ni}} = 2.3 \text{ \AA}$, the packing fraction of Fe–7Cr–21Ni is determined to be 0.5 at 1750 K and the value decreases with increasing Cr concentration, reaching 0.497 for Fe–16Cr–12Ni. This result is consistent with the variation of the excess volume with Cr concentration.

Furukawa⁴² suggested that the effective HS diameter is approximately $r_1/1.145$ for most liquid metals; here, r_1 is the nearest interatomic distance directly obtained from the experimental data. By

using the effective HS diameters of Fe, Cr, and Ni proposed by Waseda and Tamaki,⁴³ $d_{\text{Fe}} = 2.25 \text{ \AA}$, $d_{\text{Cr}} = 2.25 \text{ \AA}$, and $d_{\text{Ni}} = 2.21 \text{ \AA}$, we have calculated the packing fraction of the 72Fe–Cr–Ni alloys at 1750 K (see Fig. 4). The packing fraction of Fe–7Cr–21Ni is 0.449, and the value decreases with increasing Cr concentration. Waseda and Tamaki^{43,44} reported that the packing fractions of liquid Fe, Cr, and Ni are 0.45, 0.44, and 0.45, respectively, by using a combination of XRD experiments and the HS model. These values are consistent with the fact that the packing fraction in Fig. 4 decreases with increasing Cr concentration and thus may be related to the origin of the positive excess volume of the 72Fe–Cr–Ni alloys.

To further investigate the behavior of excess volume of the 72Fe–Cr–Ni alloys, *in situ* synchrotron XRD experiments were conducted using EML at the German synchrotron facility DESY. Upon cooling, XRD patterns were recorded continuously with the high sampling rate of 250 Hz. Ten images were merged to obtain the sufficient intensity required for calculation of the structure factors. Figure 5(a) shows the total Faber–Ziman⁴⁵ structure factors $S(q)$ of Fe–12Cr–16Ni and Fe–16Cr–12Ni obtained from the measured XRD patterns at 1750 K, which correspond to the high and low packing fraction in Fig. 4, respectively. Due to similar x-ray scattering abilities of Fe, Cr, and Ni, the total structure factor could be considered as an approximate of the Bhatia–Thornton partial structure factor S_{NN} ⁴⁶ that describes the topological structure of the melt. Although the structure factors are rather similar, a slight decrease in the intensity of the first peak and increase in its characteristic width Δq^* upon increasing Cr content from 12 at. % to 16 at. % can be observed [see the inset in Fig. 5(a) and Fig. S3 and Table SII in the supplementary material].

For single-component melts, in general, the width of the first peak on $S(q)$ is proportional to the coherently scattering domain size and thus characterizes the short-range order of the melts. This may not necessarily hold for multicomponent melts as the total structure factor is a combination of the partial structure factors. As Fe, Cr, and Ni have very similar atomic radii, it could be supposed that the partial structure factors in Fe–Cr–Ni melts are also very similar, at least what concerns the first maximum. Based on this assumption, it can be supposed that the addition of Cr decreases the degree of

FIG. 4. Packing fraction of the 72Fe–Cr–Ni alloys as a function of Cr concentration at 1750 K. Errors indicate the standard deviation.

FIG. 5. (a) Total structure factors $S(q)$ of Fe–12Cr–16Ni and Fe–16Cr–12Ni at 1750 K. The inset illustrates an example of how the Δq^* is determined in the $S(q)$ profile. (b) Pair distribution functions $g(r)$ (PDF) of Fe–12Cr–16Ni and Fe–16Cr–12Ni deduced from the $S(q)$ at 1750 K. The inset shows the parts of $g(r)$ functions used for calculations of coordination numbers.

topological ordering in the 72Fe–Cr–Ni melts in a manner which is consistent with the influence of Cr on their excess volume and packing fraction.

The pair distribution functions (PDF) $g(r)$ of Fe–12Cr–16Ni and Fe–16Cr–12Ni calculated from the corresponding structure factors are shown in Fig. 5(b). An averaged total coordination number (CN) is obtained from the $g(r)$ by integration as follows:

$$CN = 4\pi\rho_o \int_{r_1}^{r_2} r^2 g(r) dr. \quad (3)$$

Here, r_1 and r_2 are the limits of the first coordination shell, defined by positions of the minima on the left- and right-hand sides of the first peak [inset in Fig. 5(b)]; ρ_o is the number density. The coordination number is determined to be 12.89 ± 0.09 for the Fe–12Cr–16Ni melt and 12.76 ± 0.03 for the Fe–16Cr–12Ni melt at 1750 K (for more details, see Fig. S4 and Table SIV in the supplementary material). It has to be admitted that the calculated difference of these CN's is rather small just about 1%. However, the trend of decreasing coordination number with increasing Cr concentration correlates with the observed increase in the molar volume.

Based on the theoretical^{47,48} and experimental studies,^{49–51} it has been accepted that a shoulder on the high- q side of the second peak of the structure factor is a characteristic signature of icosahedral short-range order (ISRO). From the first peak position (q_1) on $S(q)$, the relative positions (q_2/q_1 and q_3/q_1) for the second peak (q_2) and the shoulder (q_3) have been characterized for the ISRO, which are 1.71 and 2.04 for a perfect icosahedron, respectively.^{47,48} Previous EML experiments with neutron scattering and MD simulation studies revealed that ISRO is found in liquid Fe and the relative positions are ~ 1.74 (q_2/q_1) and 2.01 (q_3/q_1), respectively.⁴⁹ Note that the relative positions for Fe–12Cr–16Ni are determined to be 1.75 ± 0.007 (q_2/q_1) and 1.98 ± 0.012 (q_3/q_1) from the measured $S(q)$ (Table SIII in the [supplementary material](#)). This value is in good agreement with the ideal value but shows a slightly larger deviation than those values of liquid Fe. Kelton *et al.*⁵⁰ reported that the relative positions for a $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ liquid are 1.72 and 1.97, respectively, indicating little distortion in the icosahedral order of the liquid. In a similar aspect, the relative positions for liquid Ni were reported to be 1.74 and 1.95, but 1.76 and 1.92 for liquid Ti, indicating distorted icosahedral order in the liquid Ti.^{39,51}

It should also be mentioned that there are works reporting on the absence of ISRO in molten alloys and even elemental liquids. For example, Holland-Moritz *et al.*⁵² reported that the SRO in liquid $\text{Ni}_{36}\text{Zr}_{64}$ differs from ISRO and BCC-like order and A15-like order were also observed in Zr^{53} and Ta^{54} liquids, respectively. A recent advanced technique using the angstrom-beam electron diffraction method revealed that the icosahedral order in a $\text{Zr}_{80}\text{Pt}_{20}$ metallic glass is geometrically distorted and inclined to form a mixed configuration, composed of a partial icosahedral symmetry and a partial FCC symmetry.⁵⁵ By using the same technique, Zhu *et al.*⁵⁶ reported that icosahedron-like and crystal-like local structures are observed in a $\text{Zr}_{70}\text{Cu}_{29}\text{Pt}_1$ metallic glass and for the partial icosahedral structure, the relative q ratios of the second peak and the shoulder to the first peak are calculated to be around 1.75 and 2.05, respectively, while the crystal-like order is not. It means that even in disordered systems with complex atomic configurations, the q ratio is still an important factor to characterize the degree of ISRO. On the basis of these structural analyses, therefore, it could be assumed that the local structure in liquid Fe may be dominated by ISRO and seems to be distorted slightly by adding Cr or Ni elements, resulting in a decrease of the degree of ISRO or an increase of non-ISRO in the 72Fe–Cr–Ni melts. These observations are consistent with the behavior of the excess volume and packing fraction with Cr concentration as shown in Figs. 3 and 4, revealing the potential origin of the positive excess volume of the 72Fe–Cr–Ni alloys. In the future, additional theoretical and MD simulation studies for the liquid structure of the 72Fe–Cr–Ni melts should be performed for a more comprehensive understanding of the origin of the positive excess volume.

V. CONCLUSIONS

In summary, the excess volume and structure of the six 72Fe–Cr–Ni melts ($7 \leq \text{Cr} \leq 16$ wt.%) have been studied using a combination of *in situ* synchrotron XRD and containerless levitation techniques. From the density evaluation, the excess volume and packing fraction of the 72Fe–Cr–Ni melts have been estimated as a function of Cr concentration, revealing that the 72Fe–Cr–Ni

alloy system exhibits a positive sign of excess volume and the packing fraction decreases with increasing Cr concentration. The analysis of structure factor and pair distribution function of the melts demonstrated that the higher packing fraction at the low Cr composition is attributed to the higher chemical and topological ordering in the 72Fe–Cr–Ni melts. Our results provide the direct correlation between excess volume and structure in metallic melts.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for additional information for the evaluation of the density and the $S(q)$ and $g(r)$ of the 72Fe–Cr–Ni melts.

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