Vibrational properties of alpha- and sigma-phase Fe-Cr alloy

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Experimental investigation as well as theoretical calculations, of the Fe-partial phonon density-of-states (DOS) for nominally Fe\textsubscript{52.5}Cr\textsubscript{47.5} alloy having (a) \(\alpha\)- and (b) \(\sigma\)-phase structure were carried out. The former at sector 3-ID of the Advanced Photon Source, using the method of nuclear resonant inelastic X-ray scattering, and the latter with the direct method [K. Parlinski et al., Phys. Rev. Lett. \textbf{78}, 4063 (1997)]. The characteristic features of phonon DOS, which differentiate one phase from the other, were revealed and successfully reproduced by the theory. Various data pertinent to the dynamics such as Lamb-Mössbauer factor, \(f\), kinetic energy per atom, \(E_k\), and the mean force constant, \(D\), were directly derived from the experiment and the theoretical calculations, while vibrational specific heat at constant volume, \(C_V\), and vibrational entropy, \(S\) were calculated using the Fe-partial DOS. Using the values of \(f\) and \(C_V\), we determined values for Debye temperatures, \(\Theta_D\). An excellent agreement for some quantities derived from experiment and first-principles theory, like \(C_V\) and quite good one for others like \(D\) and \(S\) was obtained.

For many years Fe-Cr alloy system has been of exceptional scientific and technological interest. The former stems on one hand from its interesting physical properties such as magnetic ones, and on the other hand from the fact that it forms a solid solution within the whole concentration range preserving, at least metastably, the same crystallographic structure (bcc). This, in turn, gives a unique chance for investigating the influence of the composition on various physical properties within the same structure as well as adequately testing different theoretical models and theories. The latter follows from the fact that Fe-Cr alloys constitute the basic ingredient of stainless steels (SS) that for a century have been one of the most important structural materials \cite{1}, and, consequently, some properties of SS are inherited from the parent alloy. To the latter belongs a \(\sigma\)-phase that can precipitate if a quasi-equatomic Fe-Cr alloy undergoes an isothermal annealing in the temperature range \(\sim 800\text{K} \leq T \leq \sim 1100\text{K}\). The \(\sigma\)-phase has a tetragonal structure (type \(D_{14}^{4h}\) \(P_{4_2}/nm\)) with 30 atoms distributed over five different sites (Table 1). Its physical properties are, in general, quite different than those of the \(\alpha\)-phase of similar composition. Some properties, like the magnetic ones, are even dramatically different \cite{2}, other properties, like the Debye temperature, seem to be very similar \cite{3}. The latter is rather unexpected as the hardness of the \(\sigma\)-phase is by a factor of \(\sim 3\) larger than that of the \(\alpha\)-phase. To clarify this situation a more detailed knowledge of vibrational properties of the \(\sigma\)- and \(\alpha\)-phases is essential. In addition, the \(\sigma\)-phase belongs to an important family of tetrahedrally close-packed Frank-Kasper phases and is one of the closest low-order crystalline approximants for dodecagonal quasicrystals which have similar local structural properties with the icosahedral glass (ICG) \cite{4}. The latter implies that the study of the vibrational properties of the \(\sigma\)-phase should shed some light on similar properties in ICGs. Challenged by this possibility and motivated by a lack of available knowledge on dynamical properties of the real \(\sigma\)-phase we have carried out both, an experimental investigation as well as theoretical calculations, of the Fe-partial phonon density-of-states (DOS) for nominally Fe\textsubscript{52.5}Cr\textsubscript{47.5} alloy having (a) \(\alpha\)- and (b) \(\sigma\)-phase structure.

The master alloy (\(\alpha\)-phase) was prepared by melting, in appropriate proportion, \(^{57}\text{Fe}\)- enriched (\(\sim 95\%\)) iron with chromium. The ingot was then cold-rolled down to a thickness of about 30\(\mu m\) from which two \(5 \times 5 \text{ mm}^2\) plates were cut out. They were next solution-treated at 1273 K for 72 h. One of the samples was afterwards transformed into the \(\sigma\)-phase by the isothermal annealing at 973 K for 7 days. The verification of the transformation into the \(\sigma\)-phase caused by such thermal procedure was done by recording a \(^{57}\text{Fe}\) Mössbauer spectrum at 295 K. Experiments were conducted at sector 3-ID of
TABLE I: Atomic crystallographic positions and numbers of NN atoms for the five lattice sites of the Fe-Cr σ-phase.

| Site | Crystallographic positions | NN Total |
|------|---------------------------|----------|
| A    | 2i (0, 0, 0)              | 4 4 12   |
| B    | 4f (0.4, 0.4, 0)          | 2 1 4 6 15 |
| C    | 8i (0.74, 0.66, 0)        | -1 5 4 4 14 |
| D    | 8i (0.464, 0.131, 0)      | 1 2 4 1 4 12 |
| E    | 8j (0.183, 0.183, 0.252)  | 1 3 4 4 2 14 |

...the Advanced Photon Source. The vibrational properties such as the Fe-partial phonon density-of-states were studied using the method of nuclear resonant inelastic X-ray scattering (NRIXS) [3, 6]. Synchrotron radiation X-rays were monochromatized to a bandwidth of 1.2 meV and tuned in energy ranges of +/- 80 meV (room temperature measurements) and -20 meV to +80 meV (measurement at 20 K) around the 57Fe nuclear transition energy of 14.4125 keV. The X-ray flux and beam size at the sample position were 4 × 10^9 photons/s and 0.3 × 2 mm^2, respectively. Data collection times were about 3 hours for the room temperature measurement of each sample and about 12 hours for the low temperature measurement of the σ-phase sample. We followed previously described evaluation procedures [3, 6] using the publicly available PHOENIX software [2]. The following quantities were derived directly from the data: Lamb-Mössbauer factor, $f$, kinetic energy per atom, $E_k$, and the mean force constant, $D$. No specific assumptions about the character of the vibrations had to be made to obtain these values. The Fe-partial DOS was derived by direct data inversion using the Fourier-Log method under the assumption of quasi-harmonic vibrations. The consistency of this procedure was verified by independent calculation of Lamb-Mössbauer factor, kinetic energy per atom, and mean force constant from the DOS and by agreement of these values with same quantities obtained directly from the data. Then the following quantities were calculated using the Fe-partial DOS: vibrational specific heat at constant volume, $C_V$, and vibrational entropy, $S$. The assignment of Debye temperatures, $\Theta_D$, is based on the Debye model, i.e., the DOS is proportional to energy squared, and they are widely used in the literature. With the determination of the Fe-partial DOS, we have surpassed the Debye model but find it useful to provide Debye temperatures for comparison. Using the values of $f$ and $C_V$, we determined commonly presented values for $\Theta_D$. In calculations, both phases of Fe-Cr alloy were modeled by the appropriate atomic configurations placed in a supercell with the periodic boundary conditions. The disordered $\alpha$-Fe$_{52.5}$Cr$_{47.5}$ alloy was approximated by the $\alpha$-Fe$_{50}$Cr$_{50}$ one, for which we used the 2 × 2 × 2 bcc cell with 16 atoms. For random distribution of atoms, there are about 500 different atomic configurations to be considered. However, for the sake of computer and time capacity, we have chosen at random only five to be included in our calculations. The real $\sigma$-Fe$_{52.5}$Cr$_{47.5}$ sample was approximated by a $\sigma$-Fe$_{53.3}$Cr$_{46.7}$ one. The latter was studied in the 1 × 1 × 1 tetragonal supercell with 30 atoms (16 Fe and 14 Cr atoms). The structure optimization was done using the spin-polarized density functional total energy calculations performed within the generalized gradient approximation (GGA) using the VASP package [8, 9]. The valence electrons for each atom (electron configuration: $d^5s^1$ and $d^8s^2$ for the Cr and Fe atoms, respectively) are represented by plane wave expansions. The wave functions in the core region are evaluated using the full-potential projector augmented-wave (PAW) method [10, 11]. The integrations in the reciprocal space were performed on the 8 × 8 × 8 and 4 × 4 × 4 grid for α- and σ- phases, respectively. During the optimization, the Hellmann-Feynman (H-F) forces and the stress tensor were calculated and the structure optimization was performed in two steps. First the lattice constants were determined assuming the appropriate symmetry, then the atomic positions were found in a fixed unit cell. The crystal structure optimization was finished when residual forces were less than 10^{-5} eV/Å and stresses were less than 0.1 kbar. The calculated lattice constants are $a = 5.64$ Å and $c = 4.74$ Å for the cubic and tetragonal symmetry, respectively. The optimized magnetic moments on the Fe atoms are ordered ferromagnetically with the average values 2.03 and 0.96 $\mu_B$, in the α and σ phases, respectively. On the Cr atoms, the antiparallel arrangement occurs with the negative mean magnetic moments -0.17 and -0.28 $\mu_B$ in the respective phases.

For the optimized structures the phonon dispersions and density of states were calculated using the direct method [12, 13]. The dynamical matrix of the crystal is constructed from the H-F forces generated while displacing atoms from their equilibrium positions. For considered structures each atom must be displaced in three directions. For the α and σ-phases, a complete set of H-F forces is obtained from 48 and 90 independent atomic displacements, respectively. The amplitude of the displacements equals 0.03 Å. To minimize systematic errors we applied displacements in positive and negative directions. Finally, the phonon frequencies are obtained by the diagonalization of the dynamical matrix for each wave vector. The phonon DOS is calculated by the random sampling on the k-point grid in the reciprocal space, and then the thermodynamic functions are obtained within the harmonic approximation.

The phonon DOS’s measured on 57Fe for both phases of the Fe-Cr alloy are presented in Figure 1. The differences in the energy range covered by the spectrum and the discrete structure of the spectrum are significant. The spectrum obtained for the α-phase is found to be similar to that of pure Fe [14] exhibiting a distinct peak...
FIG. 1: (Color online) Phonon DOS as measured on $^{57}$Fe atoms at 298 K for the $\alpha$- (circles) and the $\sigma$-phase (triangles) on the Fe$_{52.5}$Cr$_{47.5}$ samples.

at 36 meV. The Fe-partial DOS spectrum of the $\sigma$-phase demonstrates the additional high-frequency peak at 40 meV, that is not observed neither in $\alpha$-FeCr nor in pure bcc-Fe. There is also the shift downward of the low-energy peak, which makes the entire spectrum broader than in the $\alpha$-phase. In Figure 2 the measured and calculated phonon DOS spectra of $\alpha$-FeCr are compared. The shape of both spectra is similar and two characteristic peaks of measured spectrum are reproduced satisfactorily. As in the chosen supercell, there are eight Fe atoms, hence by taking into account five different atomic configurations, one considers vibrations of forty independent Fe atoms. Their partial DOS turned out to be different, but their shape was not correlated with the particular nearest-neighbor (NN) - next NN shell. Consequently, the final DOS was calculated using the partial contributions with the same weights. The discrepancies between measured and calculated spectra are likely caused by an incomplete representation of possible atomic configuration of FeCr disordered alloy in our model.

Likewise, the calculations of $\sigma$-FeCr performed for only one configuration yield the phonon DOS exhibiting characteristic features of the experimental spectrum (Figure 3). Observed discrepancies, like underestimation of the intensity of low-frequency peak or shift of high-frequency peak, are not significant. Using the theoretical result, it is feasible to separate the individual contributions to the total DOS generated by the Fe atom placed at each particular crystallographic position.

Thus, we see that the Fe atoms on sites A and C are causing the high-energy contributions to the DOS. The NN sites of these Fe atoms are placed at distances shorter than 2.48Å. In pure bcc-Fe, all 8 NN atoms are situated at the same distance of 2.485Å. The shorter distances between atoms result in the larger interatomic interaction. Therefore, in $\sigma$-FeCr, the phonon frequencies higher than 40 meV, which is a high-frequency limit of bcc-Fe DOS spectrum, are observed. Also due to larger dispersion of distances in the $\sigma$-phase, its phonon spectrum is much broader than in the $\alpha$-phase, where the atomic positions are very close to those of the pure bcc-Fe.

FIG. 2: (Color online) Phonon DOS as measured on $^{57}$Fe atoms at 298 K (circles) and as calculated (dotted line) for the $\alpha$-Fe$_{52.5}$Cr$_{47.5}$.

FIG. 3: (Color online) Phonon DOS as measured on $^{57}$Fe atoms at 298 K on the $\sigma$- Fe$_{52.5}$Cr$_{47.5}$ sample (triangles) and as calculated (dotted line). DOS-curves for particular crystallographic sites are indicated, too.

The data derived from the experiment and the theoretical calculations are displayed in Table I. One can see a very good agreement for some quantities like specific heat and quite good for other ones like force constant and entropy. The values of the Debye temperature derived from the specific heat are close to those calculated from the Lamb-Mössbauer factor, and there is a small difference for this quantity found for different phases. These findings disagree with experimentally found $\Theta_D$-values for the two phases using second-order Doppler shifts from Mössbauer spectroscopy. In those studies, the $\Theta_D$-values for the $\alpha$-phase were larger than the ones for the $\sigma$-phase. This apparent discrepancy is explained by the
fact that the center shift measured by Mössbauer spectroscopy constitutes a sum of the chemical isomer shift, which is independent on the atomic motion, and the second-order Doppler shift, which is a relativistic correction to the atomic energy levels purely due to motion. The second-order Doppler shift is proportional to the vibrational kinetic energy of the $^{57}$Fe atom [15], i.e. SOD[mm/s] = -0.00565×$E_k$[meV]. Only under the assumption that the chemical isomer shift is temperature independent, the Mössbauer measurement can provide the correct Debye temperature. This does not seem to be the case here, and our NRIXS data present a notable improvement in the understanding of the role of vibrations in the Fe-Cr system. The value of the vibrational entropy measured at 298 K for the $\alpha$-phase agrees quite well with inelastic neutron scattering results on samples of similar composition [14]. Also the difference in the entropy values, $\Delta S = S_\sigma - S_\alpha = 0.095 \pm 0.009 k_B$ as determined in the present experiment from the Fe-partial DOS agrees well with the corresponding difference calculated from the equation $\Delta S = 3 k_B \ln(\Theta_D/\Theta_D) = 0.07 k_B$, where $k_B$ is the Boltzmann constant and $\Theta_D$ is the Debye temperature as determined from the second-order Doppler shift for the $\alpha$ ($i = \alpha$) and the $\sigma$ ($i = \sigma$) phase, respectively [15]. The corresponding theoretical value of $\Delta S$ is equal to 0.058 $k_B$. Taking into account the approximations used in the calculations, the agreement seems to be quite satisfactory.

In summary, we have revealed, both experimentally and theoretically, significant differences in the partial-Fe phonon DOS of the $\alpha$ and $\sigma$ phases of a quasi-atomistic Fe-Cr alloy. Although, the sigma phase is a very complex object due to a high number of atoms per unit cell, five different sublattices with high coordination numbers (12-15), each showing chemical disorder, which altogether results in a huge number of possible atomic configurations, it was described reasonable well in terms of only one adequately chosen configuration. From the calculations, it is also evident that the dynamics in particular sublattices is different. The method was also successfully used to calculate the dynamics of the disordered alloy in the alpha-phase. Although its crystallographic structure is much simpler, but, due to the chemical disorder, the number of possible atomic configurations is high, making the calculations not trivial. We have also obtained relevant thermodynamic quantities without necessity of using empirical parameters. Such a complex alloy has been studied for the first time within the combined NRIXS and theoretical $ab$ initio approach, and it may provide understanding of lattice dynamics in a wide variety of disordered systems.

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**TABLE II: Physical quantities derived from the measured and calculated Fe-partial DOS. The units are meV/atom for vibrational kinetic energy, $E_k$; $k_B$/atom for vibrational entropy, $S$; and specific heat $C_V$; N/m for mean force constant, $D$; K for Debye temperatures, $\Theta_D$.**

| quantity     | experiment | theory |
|--------------|------------|--------|
| $E_k@298K$   | 0.782±0.001 | 0.768±0.002 |
| $E_k@298K$   | 42.4±0.1   | 41.4±0.2   |
| $D@298K$     | 156±1      | 157±2      |
| $C_V@298K$   | 2.747±0.006 | 2.748±0.007 |
| $S@298K$     | 3.252±0.006 | 3.347±0.007 |
| $f@20K$      | 0.915±0.0002 | 0.915±0.0002 |
| $E_k@20K$    | 18.93±0.06 | 18.93±0.06 |
| $D@20K$      | 155.1±0.7  | 155.1±0.7  |
| $f@0K$       | 0.919±0.0001 | 0.9149±0.0003 |
| $E_k@0K$     | 19.32±0.07 | 19.32±0.07 |
| $\Theta_D(f@298K)$ | 417 | 398 |
| $\Theta_D(C_V)$      | 399    | 398    |
| $\Theta_D(f@20K)$    | 387    | 387    |
| $\Theta_D(f@0K)$     | 403    | 385    |

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