

## Vibrational Properties of $\alpha$ - and $\sigma$ -Phase Fe-Cr Alloy

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Experimental and theoretical studies, of the Fe-partial phonon density of states (PDOS) for Fe<sub>52.5</sub>Cr<sub>47.5</sub> alloy having  $\alpha$  and  $\sigma$  phases were carried out. The former using the nuclear resonant inelastic x-ray scattering method, and the latter with the direct one. Characteristic features of PDOS, which distinguish one phase from the other, were revealed and successfully reproduced by the theory. Data pertinent to the dynamics such as the Lamb-Mössbauer factor,  $f$ , the kinetic energy per atom,  $E_k$ , and the mean force constant,  $D$ , were directly derived, while vibrational specific heat at constant volume,  $C_V$ , and vibrational entropy,  $S$  were calculated using the Fe partial PDOS. Based on the values of  $f$  and  $C_V$ , we determined Debye temperatures,  $\Theta_D$ . An excellent agreement for some quantities derived from experiment and first-principles theory, like  $C_V$  and quite good ones for others like  $D$  and  $S$  were obtained.

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For many years, the Fe-Cr alloy system has been of exceptional scientific and technological interest. The alloy shows interesting physical properties such as magnetism and forms a solid solution within the whole concentration range preserving, at least metastable, the same crystallographic structure (bcc). This, in turn, gives a unique chance to investigate the effect of the composition on various physical properties within the same structure as well as to adequately test different theoretical models and theories. In fact, Fe-Cr alloys constitute the basic ingredient of stainless steels that for a century have been one of the most important structural materials [1], and, hence, some properties of stainless steels are inherited from the parent alloy. A  $\sigma$  phase can precipitate if a quasiequiatom Fe-Cr alloy undergoes an isothermal annealing in the temperature range of  $\sim 800 \text{ K} \leq T \leq \sim 1100 \text{ K}$ . It has a tetragonal structure (type  $D_{4h}^{14} P4_2/mnm$ ) with 30 atoms distributed over five different sites (Table I). Its physical properties are, in general, quite different than those of the  $\alpha$  phase of similar composition. Some experimentally found behavior, such as magnetic properties, is even dramatically different [2]. Other properties, such as the Debye temperature,  $\Theta_D$ , seem to be very similar [3]. The similarity of  $\Theta_D$  values is rather unexpected because the hardness of the  $\sigma$  phase is larger by a factor of  $\sim 3$  than that of the  $\alpha$  phase. To clarify this point, 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 [4]. The study of the vibrational properties of the  $\sigma$  phase therefore should shed some light on similar properties in icosahedral glass. 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<sub>52.5</sub>Cr<sub>47.5</sub> alloy having  $\alpha$ - and  $\sigma$ -phase structure.

The master alloy ( $\alpha$  phase) was prepared by melting, in appropriate proportion, <sup>57</sup>Fe-enriched ( $\sim 95\%$ ) iron with chromium. The ingot was then cold rolled down to a thickness of about 30  $\mu\text{m}$  from which two  $5 \times 5 \text{ mm}^2$  plates were cut out. The plates were then solution treated at 1273 K for 72 h. Afterwards one of the samples was transformed into the  $\sigma$  phase by the isothermal annealing at 973 K for 7 days. The change into the  $\sigma$  phase was verified by recording a <sup>57</sup>Fe Mössbauer spectrum at 295 K. Experiments were conducted at sector 3-ID of the Advanced Photon Source [5,6]. The vibrational properties such as the Fe partial phonon DOS were studied using the method of nuclear resonant inelastic x-ray scattering (NRIXS) [6,7]. Synchrotron radiation x-rays were monochromatized to a bandwidth of 1.2 meV and tuned in

TABLE I. Atomic crystallographic positions, Fe occupancy of sublattices,  $N_{\text{Fe}}$ , and numbers of NN atoms for the five lattice sites of the Fe-Cr  $\sigma$  phase.

Site	Crystallographic positions	$N_{\text{Fe}}$	NN					Total
			A	B	C	D	E	
A	$2i(0, 0, 0)$	2	$\cdots$	4	$\cdots$	4	4	12
B	$4f(0.4, 0.4, 0)$	1	2	1	2	4	6	15
C	$8i(0.74, 0.66, 0)$	3	$\cdots$	1	5	4	4	14
D	$8i(0.464, 0.131, 0)$	7	1	2	4	1	4	12
E	$8j(0.183, 0.183, 0.252)$	3	1	3	4	4	2	14

energy ranges of  $\pm 80$  meV (measurements at 298 K) and  $-20$  to  $+80$  meV (measurement at 20 K) around the  $^{57}\text{Fe}$  nuclear transition energy of 14.4125 keV. The x-ray flux and beam size at the sample position were  $4 \times 10^9$  photons/s and  $0.3 \times 2$  mm<sup>2</sup>, respectively. Data collection times were about 3 h for the 298 K measurement of each sample and about 12 h for the 20 K measurement of the  $\sigma$ -phase sample. We followed previously described evaluation procedures [6,7] using the publicly available PHOENIX software [8]. 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 get these values. The Fe partial DOS was derived by direct data inversion using the Fourier-Log method under the assumption of quasiharmonic vibrations. The consistency of this procedure was verified by independent calculation of  $f$ ,  $E_k$ , and  $D$  from the DOS and by agreement of these values with the same quantities obtained directly from the data. The calculation of the three quantities from moments or DOS utilize different energy regions of the data. Hence the agreement provides sufficient confidence in our choice of energy range and in the reliability of the values within the statistical errors of the data. The following quantities were calculated using the Fe partial DOS: vibrational specific heat at constant volume,  $C_V$ , vibrational entropy,  $S$ , and Debye sound velocity,  $v_D$ . The Debye sound velocity was derived from the low-energy part of the DOS, which approximates parabolic shape [9], using a refined extrapolation procedure [10]. The assignment of Debye temperatures 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  $\Theta_D$  for comparison. Using the values of  $f$  and  $C_V$ , we determined commonly presented values for  $\Theta_D$ .

In the calculations, both phases of Fe-Cr alloy were modeled by the appropriate atomic configurations placed in a supercell with periodic boundary conditions. The disordered  $\alpha$ -Fe<sub>52.5</sub>Cr<sub>47.5</sub> alloy was approximated by the  $\alpha$ -Fe<sub>50</sub>Cr<sub>50</sub> composition, for which we used a  $2 \times 2 \times 2$  bcc cell with 16 atoms. For random distribution of atoms, about 500 different atomic configurations should be considered in principle. However, limited computing resources resulted in the inclusion of just five configurations that were chosen randomly. The real  $\sigma$ -Fe<sub>52.5</sub>Cr<sub>47.5</sub> sample was approximated by a  $\sigma$ -Fe<sub>53.3</sub>Cr<sub>46.7</sub> composition which was studied using a  $1 \times 1 \times 1$  tetragonal supercell with 30 atoms (16 Fe and 14 Cr atoms, the distribution of Fe over the sites is given in Table I). Structure optimization was achieved by spin-polarized density functional total energy calculations performed within the generalized gradient approximation using the VASP package [11]. The valence electrons for each atom (electron configuration:  $d^5s^1$  and  $d^6s^2$  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 method [12,13]. Integrations in reciprocal space were performed on a  $8 \times 8 \times 8$  and  $4 \times 4 \times 4$  grid for the  $\alpha$  and  $\sigma$  phase, respectively. Structure optimization was performed as follows. The lattice constants were determined assuming the appropriate symmetry, then the atomic positions were found in the fixed-size unit cell. This procedure was repeated until 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  $a = 8.60$  Å,  $c = 4.74$  Å for the cubic and tetragonal symmetry, respectively. The optimized magnetic moments of the Fe atoms are ordered ferromagnetically with average values of  $1.88$  and  $0.96\mu_B$  in the  $\alpha$  and  $\sigma$  phase, respectively. The magnetic moments of the Cr atoms are in antiparallel arrangement with average values of  $-0.013$  and  $-0.28\mu_B$ , respectively. From these values, average magnetic moments of  $0.38\mu_B$  for the  $\sigma$  phase and  $0.95\mu_B$  for the  $\alpha$  phase were derived. The  $\sigma$ -phase value compares rather well with results of others for similar compositions [14,15]. The differences likely follow from unlike atomic configurations taken into account in these studies.

For the optimized structures, the phonon dispersions and DOS were calculated with the direct method [16,17]. The dynamical matrix of the crystal was constructed from the Hellmann-Feynman forces generated while displacing atoms from their equilibrium positions. Each atom must be displaced in three directions, and a complete set of Hellmann-Feynman forces was obtained from 48 and 90 independent atomic displacements for the  $\alpha$  and  $\sigma$  phase, 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 were obtained by the diagonalization of the dynamical matrix for each wave vector. The phonon DOS was calculated by the random sampling of the  $k$ -point grid in reciprocal space, and then the thermodynamic functions were obtained within the harmonic approximation.

The phonon DOS measured on  $^{57}\text{Fe}$  for both phases of the Fe-Cr alloy and are presented in Fig. 1(a). The differences in the energy range covered by the spectra and their discrete structure are significant. The DOS obtained for the  $\alpha$  phase is found to be similar to that of pure Fe [18] showing a distinct peak at 36 meV. The Fe partial DOS spectrum of the  $\sigma$  phase has an additional high-frequency peak at 40 meV that is observed neither in  $\alpha$  Fe-Cr nor in pure bcc Fe. In addition, the downward shift of the low-energy peak broadens the entire spectrum compared to the  $\alpha$  phase. In Fig. 1(b) the measured and calculated phonon DOS of  $\alpha$  Fe-Cr are compared. The shape of both spectra is similar and two characteristic peaks of measured spectrum are reproduced adequately. The eight Fe atoms of the chosen supercell in combination with five various atomic configurations produce 40 independent contributions to the

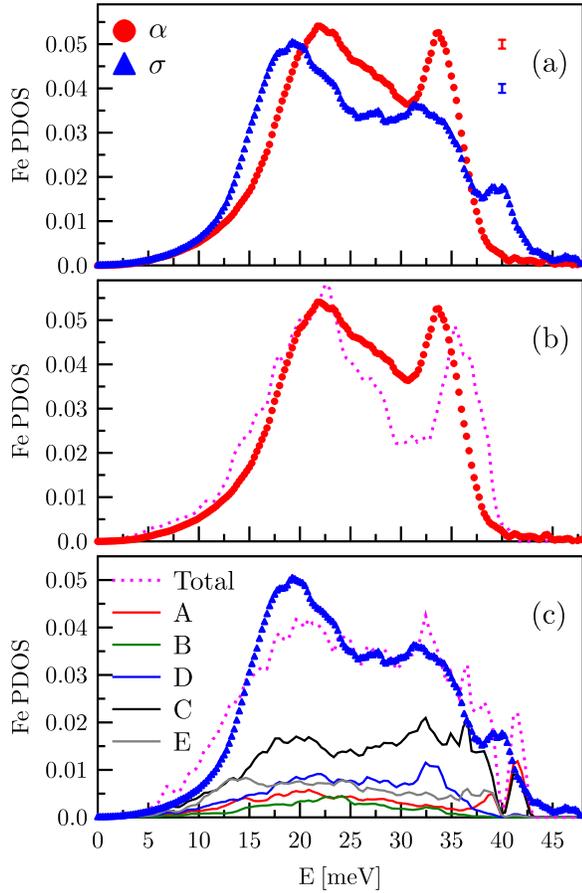


FIG. 1 (color online). (a) Phonon DOS as measured on  $^{57}\text{Fe}$  atoms at 298 K for the  $\alpha$  (circles) and the  $\sigma$  phase (triangles) of the  $\text{Fe}_{52.5}\text{Cr}_{47.5}$  samples. Maximum error bars are shown; (b) measured (circles) and calculated (dots) DOS for the  $\alpha$ - $\text{Fe}_{52.5}\text{Cr}_{47.5}$ ; (c) measured (triangles) and calculated (dots) DOS for the  $\sigma$ - $\text{Fe}_{52.5}\text{Cr}_{47.5}$ . DOS-curves for particular crystallographic sites are indicated, too.

DOS which turned out to be different, but their shape was not correlated with the particular nearest-neighbor (NN) or 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 configurations of Fe-Cr disorder in our model.

Likewise, the calculations of  $\sigma$  Fe-Cr performed for only one configuration yield the phonon DOS exhibiting characteristic features of the experimental spectrum [Fig. 1(c)]. Observed discord, such as underestimation of the intensity of the low-frequency peak or the shift of the high-frequency peak, is not significant. The theoretical result permits to separate individual contributions to the DOS generated by Fe atoms placed at each particular crystallographic position. For example, 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 2.48 Å, whereas in pure

bcc Fe, all 8 NN atoms are situated at the same distance of 2.485 Å. The shorter distances result in larger interatomic interaction, and phonon frequencies higher than 40 meV are observed in  $\sigma$  Fe-Cr but not in bcc Fe. Also the larger dispersion of distances in the  $\sigma$  phase cause the DOS to broaden in comparison to the  $\alpha$  phase where the atomic positions are very close to those of bcc Fe.

The data derived from the experiment and the theoretical calculations are displayed in Table II. The values of  $\Theta_D$  derived from the specific heat are close to those calculated from the Lamb-Mössbauer factor, and they differ little for different phases. These findings disagree with  $\Theta_D$  values derived from second-order Doppler shifts of Mössbauer spectroscopy measurements [3]. In those studies, the  $\Theta_D$  values for the  $\alpha$  phase were larger. 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 of the atomic motion, and the second-order Doppler (SOD) shift, which is a relativistic correction to the atomic energy levels purely due to motion. The SOD shift is proportional to the vibrational kinetic energy of the  $^{57}\text{Fe}$  atom, i.e.,  $\text{SOD}(\text{mm/s}) = -0.00565 \times [E_k(\text{meV})]$  [19]. Only under the assumption that the chemical isomer shift is temperature independent, the Mössbauer measurement can provide the correct value of  $\Theta_D$ . 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 Debye sound velocity of the  $\sigma$  phase exceeds the value for the  $\alpha$  phase by about 2.5% which is mostly due to the used densities of  $\rho_\alpha = 8 \text{ g/cm}^3$  and  $\rho_\sigma = 7.68 \text{ g/cm}^3$  from the calculations. An average elasticity defined by  $\rho v_D^2$  is virtually identical for the different crystal structures but about 8% higher than the value for bcc Fe with  $v_D = 3.49(5) \text{ km/s}$  and  $\rho = 8 \text{ g/cm}^3$  (including enrichment). This result is consistent with the almost identical  $\Theta_D$  values derived from the specific heat. It also suggests that for Fe-Cr alloys average elasticity or Debye temperatures are poor indicators for hardness.

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 [18]. Also the difference in the entropy values,  $\Delta S = S_\sigma - S_\alpha = (0.095 \pm 0.009)k_B$  as found in the present experiment from the Fe-partial DOS agrees well with the corresponding difference calculated from the equation  $\Delta S = 3k_B \ln(\Theta_{D\sigma}/\Theta_{D\alpha}) = 0.07k_B$ , where  $k_B$  is the Boltzmann constant and  $\Theta_{D_i}$  is the Debye temperature as determined from the SOD shift for the  $\alpha$  ( $i = \alpha$ ) and the  $\sigma$  ( $i = \sigma$ ) phase, respectively [3]. The corresponding theoretical value of  $\Delta S$  is equal to  $0.058k_B$ . Taking into account the approximations used in the calculations, the agreement seems to be quite satisfactory, all the more so the presently found values of  $\Delta S$  are remarkably close to the value of the difference in entropy for elemental Fe and Cr as found by a combination of *ab initio* and CALPHAD approach [20].

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  $D$ , km/s for Debye sound velocity  $v_D$ , K for Debye temperature  $\Theta_D$ .

Quantity	Experiment		Theory	
	$\alpha$	$\sigma$	$\alpha$	$\sigma$
$f$ at 298 K	$0.782 \pm 0.001$	$0.768 \pm 0.002$		
$E_k$ at 298 K	$42.4 \pm 0.1$	$41.4 \pm 0.2$		
$D$ at 298 K	$156 \pm 1$	$157 \pm 2$	149.41	150.59
$C_V$ at 298 K	$2.747 \pm 0.006$	$2.748 \pm 0.007$	2.746	2.752
$S$ at 298 K	$3.252 \pm 0.006$	$3.347 \pm 0.007$	3.354	3.412
$v_D$ at 298 K	$3.63 \pm 0.02$	$3.72 \pm 0.02$		
$f$ at 20 K		$0.9150 \pm 0.0002$		
$E_k$ at 20 K		$18.93 \pm 0.06$		
$D$ at 20 K		$155.1 \pm 0.7$		
$v_D$		$3.87 \pm 0.04$		
$f$ at 0 K	$0.9194 \pm 0.0001$	$0.9149 \pm 0.0003$		
$E_k$ at 0 K	$19.32 \pm 0.07$	$18.95 \pm 0.06$		
$\Theta_D(f$ at 298 K)	417	398		
$\Theta_D(C_V)$	399	398		
$\Theta_D(f$ at 20 K)		387		
$\Theta_D(f$ at 0 K)	403	385		

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 quasiequatomic Fe-Cr alloy. The  $\sigma$  phase is a very complex structure due to a high number of atoms per unit cell and five different sublattices with high coordination numbers (12–15), each showing chemical disorder, which altogether results in a huge number of possible atomic configurations. Nevertheless the DOS was described reasonably well in terms of only one adequately chosen configuration. From the calculations, it is also evident that the dynamics, in particular, sublattices are different. The method was also successfully used to calculate the dynamics of the disordered alloy in the  $\alpha$  phase. Even though its crystallographic structure is much simpler, the number of possible atomic configurations is still high due to the chemical disorder rendering the calculations nontrivial. 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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- [1] K. H. Lo, C. H. Shek, and J. K. L. Lai, *Materials Sci. Eng. R: Reports* **65**, 39 (2009).
- [2] J. Cieslak, M. Reissner, W. Steiner, and S. M. Dubiel, *Phys. Status Solidi A* **205**, 1794 (2008).
- [3] J. Cieslak, B. F. O. Costa, and S. M. Dubiel, *J. Phys. Condens. Matter* **18**, 10899 (2006).
- [4] S. I. Simdyankin, S. N. Taraskin, M. Dzugutov, and S. R. Elliott, *Phys. Rev. B* **62**, 3223 (2000).
- [5] J. Zhao *et al.*, *High Press. Res.* **24**, 447 (2004).
- [6] W. Sturhahn, *J. Phys. Condens. Matter* **16**, S497 (2004).
- [7] W. Sturhahn *et al.*, *Phys. Rev. Lett.* **74**, 3832 (1995).
- [8] W. Sturhahn, *Hyperfine Interact.* **125**, 149 (2000).
- [9] M. Y. Hu *et al.*, *Phys. Rev. B* **67**, 094304 (2003).
- [10] J. M. Jackson, E. M. Hamecher, and W. Sturhahn, *Eur. J. Mineral.* **21**, 551 (2009).
- [11] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996); *Comput. Mater. Sci.* **6**, 15 (1996).
- [12] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [13] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [14] E. A. Kabliman, A. A. Mirzoev, and A. L. Udovskii, *Phys. Met. Metallogr.* **108**, 435 (2009).
- [15] J. Pavlů, J. Vřešťál, and M. Šob, *Intermetallics* **18**, 212 (2010).
- [16] K. Parlinski, Z. Q. Li, and Y. Kawazoe, *Phys. Rev. Lett.* **78**, 4063 (1997).
- [17] K. Parlinski, computer code PHONON, Krakow, 2008.
- [18] M. S. Lucas, M. Kresch, R. Stevens, and B. Fultz, *Phys. Rev. B* **77**, 184303 (2008).
- [19] W. Sturhahn and A. I. Chumakov, *Hyperfine Interact.* **123–124**, 809 (1999).
- [20] J. Houserova, M. Friák, M. Šob, and J. Vřešťál, *Comput. Mater. Sci.* **25**, 562 (2002).