Effect of magnetism on the lattice dynamics in the $\sigma$-phase FeCr alloys

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Abstract – Anomalies in the temperature dependences of the recoil-free factor, $f$, and the average center shift, $\langle CS \rangle$, measured by $^{57}$Fe Mössbauer spectroscopy, were observed for the first time in the archetype of the $\sigma$-phase alloys system, FeCr. In both cases the anomaly started at the temperature close to the magnetic ordering temperature, and in both cases it was indicative of lattice vibrations hardening. As no magnetostrictive effects were found, the anomalies seem to be entirely due to a spin-phonon coupling. The observed changes in $f$ and in $\langle CS \rangle$ were expressed in terms of the underlying changes in the potential, $\Delta E_p$, and the kinetic energy, $\Delta E_k$, respectively. The former, with the maximum value larger by a factor of six than the latter, decreases, while the latter increases with $T$. The total mechanical-energy change, $\Delta E$, was, in general, not constant, but it resembled that of $\Delta E_p$. Only in the range of 4–15 K, $\Delta E$ was hardly dependent on $T$. The decrease of $\Delta E$ on lowering $T$ can be interpreted as an increase of the spin-phonon coupling.

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A thorough knowledge and good understanding of atomic lattice vibrations in solids, in general, and in technologically important materials, in particular, are essential, for the proper understanding of their physical properties such as thermal conductivity, heat capacity, vibrational entropy, Debye temperature, electron-phonon coupling as well as the noise of electronic devices. One of the open questions in the field is a possible relationship between magnetism and the lattice vibrations. The contribution of an electron-phonon interaction to magnetization of metallic systems is expected to be small, as, in general, $\frac{\hbar \omega_D}{E_F}$ is of the $10^{-2}$ order [1], where $\omega_D$ is the Debye cut-off frequency and $E_F$ is the Fermi energy. Consequently, the effect of magnetism on the lattice dynamics in such systems should be rather negligible. However, following Kim [1] the effect of the electron-phonon coupling can be strongly enhanced below the Curie temperature, $T_c$, in an itinerant ferromagnet. A good candidate for verifying these predictions seem to be represented by $\sigma$-FeCr alloys which are believed to be itinerant ferromagnets with $T_c$ values below 50 K [2].

The $\sigma$-phase constitutes a broad class of binary and ternary alloy systems with common crystallographic structure ($D_{14}^{\text{h}}$- $P4_2/mnm$) and physical properties depending on the system [3]. The $\sigma$-FeCr which was discovered in 1923 [4] and identified in 1954 [5] has been known not only as the archetype of the $\sigma$-phase, but mainly for scientific and technological reasons. The former stems from its interesting physical properties (e.g., complex crystallographic structure, high brittleness and hardness, low-temperature magnetism and unusually high value of the specific heat). The latter follows from the deteriorating effect of the phase presence on mechanical and corrosive properties of ferritic stainless steels that are regarded as important construction materials. Despite the phase has been known for over a half of a century, only few papers relevant to its lattice vibrational properties have been published so far [6–8]. The Fe-partial phonon density of states (PDOS) of the $\sigma$-FeCr was found to be significantly different from that of the $\alpha$-FeCr, which was not the case for the Debye temperatures of the two phases [8]. In this letter evidence obtained from the Mössbauer spectroscopic (MS) study is reported to show that magnetism can significantly affect the lattice dynamics in the $\sigma$-phase FeCr samples.
MS is an exceptionally well-suited tool to study the atomic vibrations in solids as it delivers relevant information via two spectral parameters, viz., the recoil-free factor, \( f \), and the center shift, \( CS \). The former is related to the mean-square amplitude of vibrations of the Mössbauer atoms, \( \langle x^2 \rangle \), through the following equation:

\[
f = \exp(-\langle x^2 \rangle k^2),
\]

where \( k \) is the wave vector of the gamma radiation. The latter is a measure of the mean-square velocity of the vibrating atoms, \( \langle v^2 \rangle \), via the second-order Doppler shift, SOD, given by

\[
\text{SOD} = -E_\gamma \langle v^2 \rangle / 2c^2,
\]

where \( E_\gamma \) is the energy of the gamma rays.

In solids with no electron-phonon coupling, the temperature dependences of both \( CS \) and \( f \) are smooth monotonic decreasing functions of \( T \). If, however, a strong enough spin-phonon coupling is present, an anomaly in the two quantities should be seen close to \( T_c \).

Two samples of the \( \sigma \)-phase FeCr alloys, viz., Fe\(_{54}\)Cr\(_{46} \) and Fe\(_{52}\)Cr\(_{48} \) were the subject of the present study. They were obtained by an isothermal annealing of the bcc master alloys at \( T = 973 \) K. A more detailed description can be found elsewhere [2]. In search of a possible effect of magnetism on the atomic vibrations, \(^{57}\)Fe Mössbauer spectra were recorded in a transmission geometry at various temperatures, \( T \), using a standard spectrometer, \(^{57}\)Co/Rh source for the \( \gamma \) 14.4 keV radiation and a flowing cryostat that enabled stabilization of \( T \) with an accuracy of \( \pm 0.1 \) K. Examples of the spectra recorded in this way can be seen in fig. 1(a). They were analyzed using three different least-square iteration procedures: A) superposition of five Lorentzian-shaped single lines having common, but temperature-dependent line width \( G \), individual amplitudes and \( CS \) values; B) distribution of the \( CS \) values; and C) transmission integral assuming the spectrum is composed of five single-line subspectra. From the temperature dependence of \( G \), as obtained with A), which can be seen in figs. 1(b), (c), the value of the magnetic ordering temperature (Curie point), \( T_c \), was determined. For Fe\(_{54}\)Cr\(_{46} \) \( T_c = 32.9 \) K and for Fe\(_{52}\)Cr\(_{48} \) \( T_c = 15.2 \) K were found. These values agree rather well with the corresponding figures of 38.9 K and 17.2 K, respectively, found from the magnetization data [9].

The temperature dependence of the average center shift, \( \langle CS \rangle \), as shown with the fitting procedure A), is shown as full circles in fig. 2(a). A smooth change of \( CS \) with \( T \), as expected from the Debye model, can be seen until \( T \) reaches a certain critical value below which a steep decrease is observed. Data obtained with a second run of measurements for Fe\(_{54}\)Cr\(_{46} \) added as open circles agree quite well with those obtained within the first run. The critical temperature at which the anomaly starts, 31.3 K and 16.3 K, for Fe\(_{54}\)Cr\(_{46} \) and Fe\(_{52}\)Cr\(_{48} \), respectively, was determined for each sample from the intersection of the curved lines, representing the behavior expected from the Debye model, with the straight lines, representing the anomalous part of the data. A good agreement between the temperatures at which the anomalies in \( \langle CS \rangle \) occur and the corresponding Curie temperatures, can be taken as evidence that the anomaly in \( \langle CS \rangle \), hence in the atomic vibrations, is related to the magnetic state of the samples. The observed anomaly has been confirmed by the results obtained with the methods B) and C) — see fig. 2(a).

A further support for the magnetic origin of the anomaly can be lend from the spectra measured at 4.2 K in

![Graph](image-url)
Effect of magnetism on the lattice dynamics in the $\sigma$-phase FeCr alloys

Fig. 2: (Color online) (a) The average center shift, $\langle CS \rangle$, vs. temperature, $T$, for the investigated samples as obtained with different fitting methods: A), B), C) for Fe$_{54}$Cr$_{46}$ and A) for Fe$_{52}$Cr$_{48}$. The solid and the dashed curved lines represent the behavior expected from the Debye model for the data obtained with the method A) for both samples. Their intersection with the skew straight lines marks the temperature at which the anomaly in $\langle CS \rangle$ starts to occur. The right-hand axis is scaled with the corresponding change of the mean-square velocity calculated from eq. (2). (b) $\ln f'$, $f'$ being a measure for the relative recoil-free fraction, vs. temperature, $T$, for the investigated samples. The Curie temperatures, as obtained for the two samples, are indicated by arrows. The data obtained with the second run are indicated by R.

an external magnetic field, $B_o$ —see fig. 3(a). These spectra were analyzed in terms of a standard hyperfine field distribution method, assuming a linear correlation between the hyperfine field and the isomer shift. The values of $\langle CS \rangle$ derived from this approach are displayed in fig. 3(b) vs. the external magnetic field, $B_o$, showing a significant dependence on $B_o$. The increase of the amplitude of $\langle CS \rangle$ with $B_o$ is equivalent to the increase of the mean-square velocity. The effect is consistent with the results found from the zero-field spectra —fig. 2(a) (a difference in $\langle CS \rangle$ values shown in figs. 2(a) and 3(b) is due to a difference in the temperature of the sources in both experiments).

Concerning now the $f$-factor, in the thin-absorber approximation, which was the case A) here, it is proportional to the spectral area, $A$. The $\ln(f')$, where $f' = A/A_o$, $A_o$ being the spectral area at 80K, is shown for both samples in fig. 2(b) vs $T$. The right-hand axis is scaled in the underlying change of the mean-square amplitude of vibrations, $\Delta \langle x^2 \rangle$, relative to its value at 80K. One can easily notice that an increase in $\ln(f')$ is observed for both samples below $T$ close to the corresponding Curie points (indicated by arrows). The increase in $f'$ on decreasing $T$ is equivalent to the decrease of the mean-square amplitude of vibrations, and it indicates a hardening of the lattice. As evidenced in fig. 2(b), the observed behaviour does not depend meaningfully on the method used to analyze the spectra.

The observed changes in $\langle v^2 \rangle$ and in $\langle x^2 \rangle$ can be also expressed in terms of underlying changes in the kinetic, $\Delta E_k$, and in the potential, $\Delta E_p$, energies of the vibrating atoms, respectively. A change in the kinetic energy with respect to its value at $T_c$ for the Fe$_{54}$Cr$_{46}$ sample obtained as an average over A), B) and C) data is presented in fig. 4(a). It is evident that below the Curie point, $T_c$, the kinetic energy increases gently reaching its maximum of ca. 4 meV at 4.2 K. Such a “non-thermodynamic” behavior could be related to the spin-phonon coupling that sets in at $T_c$ and it becomes stronger as $T$ decreases.

The change of the potential energy in the harmonic approximation, $\Delta E_p = 0.5D\Delta \langle x^2 \rangle$, can be estimated using for $D$ (a spring constant) the value of 155 N/m as found elsewhere [8]. The results obtained for the Fe$_{54}$Cr$_{46}$ sample as an average over A), B), and C) data are shown in fig. 4(b). It can be seen that $\Delta E_p$ shows an opposite trend with respect to that shown by $\Delta E_k$: it starts to decrease at $T$ close to $T_c$. At $T$ equal to about 15 K, $\Delta E_p$ reaches the value of about 2 meV, which hardly depends on $T$ for its lower values.

Knowing changes in both forms of the mechanical energy, one can calculate a change of the total mechanical energy of the atomic vibrations, $\Delta E = \Delta E_k + \Delta E_p$, for the temperature range of interest. The behavior of $\Delta E$ —see fig. 4(c), resembles that of $\Delta E_p$, i.e., it decreases rather steeply in the range of $\sim 33 K < T < \sim 15 K$, becoming fairly constant at lower $T$. This kind of behavior follows from the fact that the dominant energetic contribution to the observed anomaly is due to the change in the potential energy. In other words, the effect of magnetism on the atomic vibrations in the studied samples manifests itself mainly via the decrease of the mean-square amplitude of vibrations, and, to a much less extent, through the accompanying increase of the mean-square velocity of these vibrations. The lack of balance between both forms of energy means that the spin-phonon coupling is energetically non-isotropic, viz., both form of energy are affected
Fig. 3: (Color online) (a) $^{57}$Fe Mössbauer spectra recorded for the $\sigma$-Fe$_{54}$Cr$_{46}$ samples in an external magnetic field, $B_o$; (b) the average center shift, $\langle CS \rangle$, vs. $B_o$ for the investigated samples. The solid line is a parabolic fit to the data. The right-hand axis is scaled in the corresponding change of the mean-square velocity calculated from eq. (2).

differently. A decrease of $\Delta E$ on lowering $T$, as evidenced in fig. 4(c), indicative of a leak of the mechanical energy from the vibrating atoms, can be interpreted as an increase of the spin-phonon interaction. Here, at $T \lesssim 15$ K, one can observe a change of behaviour, viz., both forms of energy are no more $T$-dependent. This change of behaviour may be related to the re-entrant character of magnetism in the $\sigma$-phase FeCr alloys [10]. If so, this might mean that the transverse component of Fe-atom spins is responsible for the spin-phonon coupling as reported here. Such behaviour is, to the best of our knowledge, unique as previously observed anomalies were different. In particular [11], using the same technique (MS) for DyFe$_3$ an anomaly in $CS$ similar to ours but an opposite one in $f$ was observed. However, in that case, the material was strongly magnetostrictive, hence the observed anomalies must not necessarily be caused by the spin-phonon coupling. In our case, no traces of the magnetostriction were observed (lattice constants did not show any anomaly, and below 100 K they were hardly dependent on $T$), hence the observed anomalies seem to be entirely related to the spin-phonon coupling.

In summary, we have revealed that both spectral quantities, viz., the center shift, $CS$, and the recoil-free fraction, $f$, exhibit a strong anomaly on entering the magnetic state in the studied samples. They both indicate a hardening of the lattice, which was, to the best of our knowledge, not observed so far. Anomalous changes in $CS$ and in $f$ were expressed in the underlying changes of the kinetic and of the potential energy of atomic vibrations, respectively, revealing a very unusual (non-thermodynamic) behavior of the former, viz., an increase with lowering temperature. This and a lack of balance between the two forms of energy ($E_p > E_k$) could be understood, if new degrees of freedom were opened below $T_c$. The opening might be related to the spin-phonon coupling that becomes operative when the sample
becomes magnetically ordered or/and placed in an external magnetic field, causing the observed lack of the mechanical-energy conservation. Measurements of PDOS at temperatures where the anomaly occurs are in progress, and they will hopefully shed more light on the issue.

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