Anomalous behavior of the Debye temperature in Fe-rich Fe-Cr alloys

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Debye temperature, $\Theta_D$, of Fe-rich Fe$_{100-x}$Cr$_x$ disordered alloys with $0 \leq x \leq 22.3$ was determined from the temperature dependence of the central shift of Mössbauer spectra recorded in the temperature range of 60 – 300 K. Its compositional dependence shows a maximum at $x \approx 5$ with a relative increase of $\sim 30\%$ compared to a pure iron. The composition at which the effect occurs correlates well with that at which several other quantities, e.g., the Curie temperature and the spin-wave stiffness coefficient, $D_0$, show their maxima, but the enhancement of $\Theta_D$ is significantly greater and comparable with the enhancement of the hyperfine field (spin-density of itinerant s-like electrons) in the studied system. The results suggest that the electron-phonon interaction is important in this alloy system.

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Fe$_{100-x}$Cr$_x$ alloys are both of scientific and technological interests. The former follows, among other, from the fact that they can be regarded as a model system for studying various magnetic properties and testing appropriate theoretical models. The latter is related to the fact that the alloys form a matrix for a production of chromium steels that, due to their excellent properties, find a wide application in industry \cite{1}. For example, the steels containing 2–20 at% Cr are regarded as good candidates for the design of structural components in advanced nuclear energy installations such as Generation IV and fusion reactors. In that range of composition, the alloys show an anomalous behaviour in that several physical quantities exhibit extreme values. However, their position and the relative value depend on the quantity. For example, the Curie temperature, $T_C$, has its maximum value at $x \approx 5$ at%, which is paralleled by a maximum in the neutron value of the spin-wave stiffness coefficient, $D_0$. However, the relative increase in $T_C$ from the pure Fe is only $\sim 1\%$ \cite{2} compared with the $\sim 10\%$ effect in the $D_0$ value \cite{3}. An enhancement was also found in the hyperfine (hf) field as measured at $^{57}$Fe nuclei \cite{4} as well as at $^{119}$Sn nuclei \cite{5}. In both cases the maximum was for $x \approx 10$ at% with the relative increase of $\sim 4\%$ for the former and $\sim 15\%$ for the latter probe nuclei. Hyperfine field is usually positively correlated with the magnetic moment, $\mu$, hence in the light of the above mentioned results, one should expect a paralleled behavior for the latter. Indeed, an increased value of $\mu$ localized at Fe site was revealed from neutron diffraction experiments \cite{6,7}. In this case the maximum occurs at $x \approx 20$ at% and its relative enhancement is equal to $\sim 7\%$. Increment of $\mu$ was predicted theoretically to exist at $x \approx 15$ at% with the relative effect of $\sim 17\%$ \cite{8}, as well as at $x \approx 5$ at% with the relative effect of $\sim 3\%$ \cite{9}, and, that of $T_C$ at $x \approx 15$ at% and with the effect of $\sim 25\%$ \cite{10}. The phenomenon in the latter was explained by the enhancement of Fe-Fe exchange coupling due to the alloying effect. The importance of magnetism in the understanding of these alloys, in general, and Fe-rich ones, in particular, also seems to be crucial in the light of recent theoretical calculations that predict a negative sign of the heat of formation of Fe-Cr alloys with Cr content less than 10–12 at% \cite{11,12} as well as those obtained with ab initio calculations combined with synergic synchrotron x-ray absorption experiments showing an anomaly at $x \approx 13$ at% \cite{12}. Also a drastic decrease in the corrosion rate with chromium content increase occurs within a concentration range of 9-13 at % \cite{13}, but its reason is not fully understood. Recent calculations based on first-principles quantum-mechanical theory shed some light on the issue. In particular, they demonstrate that within this concentration range there is a transition between two surface regimes: for bulk Cr content greater than $\sim 10$ at% the Cr-rich surfaces become favorable while for a lower concentration the Fe-rich ones prevail \cite{14}. According to the authors of Ref. \cite{14} they are related with two competing magnetic effects: the magnetically induced immiscibility gap in bulk Fe-Cr alloys and the stability of magnetic surfaces. In addition, the authors show that other theoretical bulk and surface properties of Fe-rich ferromagnetic Fe-Cr alloys have their minima viz. effective chemical potential at $x \approx 15$ at%, and the mixing enthalpy at $x \approx 4$ at% \cite{14}. The latter concentration coincides well with that at which a change in the sulphidation preference takes place \cite{14}.

For the complete, or at least, a better understanding of all these effects and their relationship, further theoretical and experimental studies are, however, necessary. Towards the latter end, we have carried out measure-
ments of the Debye temperature, $\Theta_D$, for $0 \leq x \leq 22.3$ in order to verify whether or not this quantity related to the dynamics of the lattice exhibits an enhancement of its value. Though it is widely believed that the possible effect of the electron-phonon interaction on the magnetism of metallic system is of no significant importance [10], because the modification of the exchange interaction or magnetization caused by the interaction should be of the order of $10^{-2}$. However, calculations by Kim [17, 18] suggest that in an itinerant-electron ferromagnet the electron-phonon interaction might be important. Including exchange interaction between electrons enhances the effect by a factor of $\sim 10$ to $\sim 100$ [17, 18]. If these calculations are correct, then a correlation between magnetic and dynamic properties should be experimentally observed. Although in the literature there are already some data on the Debye temperature in the Fe-Cr system, they are not conclusive in that respect as they were measured in a very narrow and low temperature range viz. 1.4 – 4.2 K [19], and, in the concentration range of interest, there are only three data points. A more detailed study of the issue was also prompted by an anomalous behavior of $\Theta_D$ found for the Cr-rich samples, and, in particular, by the smallest value of $\Theta_D$ for the most Cr-rich alloy.

For the present study previous samples were used [1, 20]. The Debye temperature was measured by means of the Mössbauer spectroscopy. For that purpose a series of Mössbauer spectra was recorded in a transmission geometry for each sample in the temperature range of 60 – 300 K using a standard spectrometer and a $^{57}$Co/Rh source of 14.4 keV gamma rays. Temperature of the samples which were kept in a cryostat were stabilized with an accuracy of $\sim 0.2$ K during measurements. Examples of the recorded spectra are shown in Figs. 1 and 2. They were fitted in two ways, I and II, to get an average value of the central shift, $<CS>$, which is the quantity of merit for determining $\Theta_D$. In way I, each spectrum was fitted assuming it consists of a number of six-line patterns subspectra, each of them corresponding to a particular atomic configuration around the probe $^{57}$Fe nucleus, $(m, n)$, where $m$ is a number of Cr atoms in the first neighbor shell (NN), and $n$ is a number of Cr atoms in the next neighbor shell (NNN). It was further assumed that the effect of neighboring Cr atoms on spectral parameters (hyperfine field, and central shift) was additive. Using this procedure, which is described elsewhere in detail [4, 5, 20], the average central shift, $<CS>$, could have been calculated. In way II, each spectrum was fitted in terms of the hyperfine field distribution method [21]. Following the experimental result [20], a linear correlation between the hf. field and the isomer shift was assumed in the fitting procedure. The Debye temperature was determined from the temperature dependence of $<CS>$:

\[<CS(T)> = IS(T) + SODS(T)\]  

where $IS(T)$ is the isomer shift and it is related to the charge density at the probe nucleus and has a weak temperature dependence [22], so it is usually approximated.
by a constant term, $IS(0)$, which is eventually composition dependent. $SODS$ is the so-called second-order Doppler shift which shows a strong temperature dependence. Assuming the whole temperature dependence of $<CS>$ goes via $SODS$ term and using the Debye model for the phonon spectrum one arrives at the following formula:

$$CS(T) = IS(0) - \frac{3kT}{2mc} \left[ \frac{3\Theta_D}{8T} + 3 \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D} \frac{x^3}{e^x - 1} dx \right]$$

(2)

where $m$ is the mass of the $^{57}$Fe nucleus, $k$ is the Boltzmann constant, $c$ is the velocity of light. Fitting equation (2) to the $<CS(T)>$ values determined in the ways I and II (whose typical temperature behavior is illustrated in Fig. 3), enabled determination of the $\Theta_D$ - values. It has turned out that within the error limit they agree well with each other, hence, for final considerations, the average, $<CS> = 0.5(<CS>_I + <CS>_II)$, between each corresponding pair has been taken. Its normalized ($\Theta_D = 429$ K was found for a pure Fe - see the Table I) dependence on Cr content, $x$, is shown in Fig. 4, where, for comparison, normalized values of other physical quantities that have maximum in the their value are shown.

From the $IS(0)$-data shown in Table I it is clear that $IS(0)$ hardly depends on $x$, hence the anomaly observed in $\Theta_D(x)$ has its full origin in $SODS$. The concentration at which the maximum occurs is similar or very close to that at which several other quantities or phenomena show anomalies, and, in particular, (a) the Curie temperature [2] and (b) the neutron value of the spin-wave stiffness coefficient, $D_0$ [3]. The increase of the former can be explained in terms of the increase of the magnetic bonding between Fe atoms [10]. However, no quantitative agreement between the enhancement factor of $T_c$ and $\Theta_D$ exists. That of the latter is significantly greater and it is rather close to the enhancement of the $^{119}$Sn-site hyperfine field, $H(0,0)$, but not to the one of the $^{57}$Fe-site hyperfine field, $H(0,0)$. As the former mostly originates from the polarization of the conduction (itin-
erant) electrons and the latter from the polarization of the core (localized) electrons, one is tempted to conclude that for the enhancement of $\Theta_D$ revealed in this study the itinerant electrons are predominantly responsible.

In other words, the change of the Debye temperature of Fe–Cr alloys in the investigated range of their composition reflects underlying change in the polarization of the conduction electrons. This in turn, can be taken as evidence that in the investigated alloy system there is a coupling between spin-polarization and the phonon spectrum. A lack of a quantitative agreement as measured in terms of the position of the maximum and the amplitude of the enhancement means that the coupling is not linear.

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