Unusual dynamics of Fe atoms in a chromium matrix

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Abstract

$^{57}$Fe site Mössbauer spectroscopy (MS) was used to investigate the dynamics of $^{57}$Fe atoms embedded in a chromium lattice as impurities. From the Mössbauer spectra recorded in the temperature range of 80–350 K, a temperature dependence of the Lamb–Mössbauer factor, $f$, was determined. The latter revealed an unusual dynamics of $^{57}$Fe atoms, namely a harmonic mode below $T \approx 145$ K with a characteristic effective Debye temperature $\Theta_{\text{eff}} \approx 190.2$ K and a strongly anharmonic one above $T \approx 145$ K. The latter mode exists in two clearly defined temperature intervals with significantly different $\Theta_{\text{eff}}$ values, namely (i) $\sim 155$ K for $145 \leq T \leq 240$ K and the record-high anharmonic coefficient $\varepsilon = -25.8 \times 10^{-4}$ K$^{-1}$, and (ii) $\sim 151$ K for $T \geq 240$ K with $\varepsilon = -14 \times 10^{-4}$ K$^{-1}$. Based on Visscher’s theory, the record-low value of the relative binding force constant for Fe atoms was determined as 0.0997 for the harmonic regime. It is suggested that the unusual dynamics observed in this study might be related to the underlying spin-, charge- and strain-density waves of chromium.

(Some figures in this article are in colour only in the electronic version)

Mössbauer spectroscopy (MS) can be readily used to study lattice dynamics through two different quantities: (i) the second-order Doppler shift, SOD, which is measurable via the center shift, CS, and (i) the Lamb–Mössbauer factor or recoil-free fraction, $f$. It must, however, be remembered that the two quantities give information on the dynamics—the former via the mean-squared displacement, $\langle x^2 \rangle$, of the emitting atoms. Consequently, values of the Debye temperature, $\Theta_D$ as determined from CS and $f$, are different. For example, in metallic iron $\Theta_D = 421 \pm 30$ K was found from SOD as against $\Theta_D = 358 \pm 18$ K from $f$ [1]. MS is especially useful in investigations of the dynamics of impurities embedded in metallic matrices. The Debye temperature, which can be determined in such experiments, is known as the effective Debye temperature, $\Theta_{\text{eff}}$, and it can give information about the binding force between the impurity and the host atom [2–5]. This kind of experiment can also give useful information on anharmonic effects that may strongly depend on the host matrix [2, 5].

In this study we will use the temperature dependence of $f = \exp(-x^2/\langle x^2 \rangle)$ to study the dynamics of $^{57}$Fe atoms embedded as impurities (concentration < 0.1 at.%) in a Cr matrix, $\kappa$ being the wavenumber for the $\gamma$-rays. Using the Debye model for the lattice dynamics, $f$ can be expressed as $f = \exp(-2W)$, where for $T > \Theta_D/2$:

$$2W = \frac{6E_R T}{\Theta_D^2}.$$  

$E_R$ being the recoil energy of an unbound emitting nucleus (equal to 22.6 K for $^{57}$Fe). Equation (1) means that, for high enough temperatures, $\ln f$ is a linear function of $T$. In Steyert and Taylor [2], based on Maradudin and Flinn calculations [6], the effect of anharmonic binding on $f$ in the case of a pure crystal can be expressed by the following formula:

$$\ln f = -\frac{6E_R T}{\Theta_D^2}(1 + \varepsilon T + \delta T^2 + \cdots).$$  

Here $\delta$ should be much smaller than $\varepsilon$ which can then be termed as the anharmonic coefficient.

The sample for the present investigation was prepared by melting elemental chromium (3N purity) and iron enriched to nearly 95% in the $^{57}$Fe isotope mixed in the correct proportion to give $\leq 0.1$ at. % Fe. The melting process, which was carried...
out in an arc furnace under a protective atmosphere of pure argon, was repeated three times to ensure better homogeneity. For Mössbauer effect measurements the ingot was ground to powder with a diamond file. $^{57}$Fe site spectra, whose typical examples were recorded sequentially at different temperatures in the range between 80 and 350 K, are shown in figure 1. They were measured very carefully, i.e. in one and the same temperature run and using the same recording conditions (the source, the drive, the detection system and geometry) in order to ensure minimum error in determining the spectral area.

To obtain the $f$ values and to take into account the absorber effective thickness the spectra were fitted with a single component, i.e. it was assumed that all probe atoms experience the same hyperfine interactions, with the main goal to best reproduce their shape, hence to determine the spectral area with the best precision. Two various modeling procedures were used, i.e. it was assumed that the probe nuclei (a) see only electrostatic monopole interactions and (b) see additionally magnetic dipole interactions. It has turned out that, using procedures (a) and (b) based on the transmission integral method, all spectra, except the one recorded at 80 K, could have been successfully fitted with similar statistical quality ($\chi^2$ values). The modeling of the 80 K spectrum was better with procedure (b), which is also understandable in the light of the magnetic properties of chromium. In the fitting procedure it was further assumed that $f$, and hence the spectral area, was proportional to the effective thickness, $t$, which was a fitting parameter. Hence $t/t_0 = f/f_0$, where $t_0$ is the effective thickness of the spectrum recorded at the lowest temperature (here 80 K). The temperature dependence of $\ln(f/f_0)$ is presented in figure 2. It is evident that three characteristic ranges can be distinguished: (A) for $T \lesssim 145$ K, where the dependence is linear, i.e. $^{57}$Fe atoms experience harmonic vibrations, (B) for $145 \text{ K} \lesssim T \lesssim 240$ K and (C) for $240 \text{ K} \lesssim T \lesssim 350$ K, where the dependence is not linear, hence anharmonic effects are important. Following the theory by Maradudin and Flinn, the data in ranges A, B and C were analyzed in terms of equation (2), i.e. the measured quantity, namely $\ln(f/f_0)$, was set to be equal to

$$-\ln(f/f_0) = \ln f_0 - \frac{6E_b T}{\Theta_D}(1 + \varepsilon T)$$

(3)

i.e. it was assumed that $\delta = 0$, hence only a quadratic function of $T$ was considered. For the range A $\varepsilon$ was also set equal to zero, i.e. only a linear temperature dependence was assumed. The first term in equation (3), i.e. $\ln f_0$, was treated as a free parameter only in range A, giving the value of $-0.315$, which agrees well with the one of $-0.318$ calculated from equation (3) for $T = 80$ K and $\Theta_D = \Theta_{\text{eff}} = 190.2$ K. The best-fit analysis of the data shown in figure 2 yielded the following results: $\Theta_{\text{eff}} = 190.2 \pm 2$ K for range A, $\Theta_{\text{eff}} = 155.1 \pm 2$ K and $\varepsilon = -24.8 \times 10^{-4}$ K$^{-1}$ for range B, and $\Theta_{\text{eff}} = 151.6 \pm 3$ K and $\varepsilon = -14 \times 10^{-4}$ K$^{-1}$ for range C. It is clear from these data that the strongest behavior is observed in range B characterized not only by the strongest anharmonicity but also by the lowest effective Debye temperature. The $\Theta_{\text{eff}}$ value of 190.2 K can be further used to determine a relative spring force constant, $r = \gamma_{\text{Fe-Cr}}/\gamma_{\text{Cr-Cr}}$. For that purpose the
CDWs and SWs, such behavior of the magnetic impurities following formula can be applied [7]:

\[ \Theta_{\text{eff}} = (M_{\text{Cr}}/M_{\text{Fe}})^{1/2}(\gamma_{\text{Fe-Cr}}/\gamma_{\text{Cr-Cr}})^{1/2}\Theta_D \]  

where \( M_{\text{Cr}} \) and \( M_{\text{Fe}} \) are the masses of the host (Cr) and the impurity atom (Fe), while \( \gamma_{\text{Fe-Cr}} \) and \( \gamma_{\text{Cr-Cr}} \) are the force constants of the impurity–host and host–host binding, respectively. \( \Theta_D \) is the Debye temperature of the host (Cr).

Thus \( r = 0.0997 \) was found for range A (harmonic regime). This is about six times less than the lowest value known up to now (for Fe impurities in palladium) [8]. The \( r \) value presently found also means that the coupling of Fe atoms in the Cr matrix is extremely weak. For range A it is a factor of \( \sim 10 \) weaker than the coupling between the host atoms themselves. On the other hand, the anharmonic effect observed in ranges B and C seems to be unusually strong if one compares the presently found \( \epsilon \) values with those determined for other matrices including chromium [2, 5]. However, in the latter case the value of \( \epsilon \) was determined as an average over a temperature range of \( 80-600 \) K with a rather large temperature step (more than \( 30 \) K) and this may be a reason for the significant difference in the \( \epsilon \) values determined in this paper and those reported elsewhere [5].

In an attempt to find an answer which might be the reason for such anomalous dynamics of Fe atoms in a Cr matrix, one has to realize that metallic chromium itself has unusual properties. In particular, its electronic and lattice structure is, below the Neél temperature of \( \sim 312 \) K, harmonically modulated, the phenomenon known as spin-density waves (SDWs), charge-density waves (CDWs) and strain waves (SWs) [9]. All these three kinds of 'waves' are coupled with each other, which certainly makes the interpretation of the results even more difficult. All the more so as there is no adequate theory that could be quantitatively used to ease the interpretation, although there are some theoretical papers pertinent to the issue [10–15]. According to [10], the effect of phase fluctuations on the lattice dynamics is different in incommensurate structures, such as that observed in chromium, than in normal ones. In particular, they reduce the mean amplitude of atom displacement and produce specially modulated fluctuations of these displacements. In other words, the dynamics of the harmonically distorted lattice itself might give rise to anomalies. In our case, the lattice not only has this kind of distortion, but additionally it is magnetic and its magnetic moments show harmonically modulated structure (SDWs). Furthermore, in our experiment one observes oscillations of the lattice indirectly, i.e. via probe Fe atoms that themselves possess magnetic moment [16].

There is a fundamental question, whether or not the dynamics of the probe atoms reflects the dynamics of the underlying lattice. The question is justified in the light of theoretical calculations on a possible effect of impurities on the SDWs [10–14]. A general conclusion from these calculations is that nonmagnetic impurities strongly pin CDWs while magnetic impurities, such as Fe, do so for SDWs (strongly means that their effect is of the order of a gap, which in the case of chromium is equal to \( \sim 0.1 \) eV). In the light of a strong coupling between SDWs, CDWs and SWs, such behavior of the magnetic impurities means that they can also influence the dynamics of the lattice.

From an experimental viewpoint, the situation seems to be not so clear, and in any case one cannot make a distinct division into nonmagnetic and magnetic impurities [17]. Concerning the former, there are such that seem to act as ideal probe nuclei, i.e. all features characteristic of the SDWs of pure chromium can be revealed using them as probes. Here tantalum [18] and cadmium [19] in PAC experiments and tin in MS measurements [20, 21] can be given as the best examples. On the other hand, nonmagnetic vanadium behaves like an SDW killer as its presence quenches the SDWs, decreasing \( T_N \) at the rate of \( \sim 20 \) K/at.%. Magnetic impurities have been revealed to have a strong effect. In particular, iron decreases \( T_N \) and simultaneously changes the character of the SDWs from incommensurate to commensurate with a critical concentration of \( \sim 2.3 \) at.%. In view of the above-described situation, one can merely speculate on the origin of the anomalies in the dynamical effects observed in this study. Below we will try to give some arguments in favor of connecting these effects with the SDWs as well as to list those facts that are opposed to such an interpretation. Concerning the former, it should first be recalled that the SDWs exist as two different phases: (i) the high temperature phase, \( 123 \) K \( \leq T \leq 312 \) K, where the polarization is perpendicular to the wavevector (TSDW) and (ii) the low temperature phase, \( T \leq 123 \) K, where the polarization is longitudinal (LSDW). It is plausible that the dynamics found in this experiment is connected with these two phases as, according to previous studies [22, 23], TSDW and LSDW phases have different magnetomechanical properties. In particular, de Morton has observed a decrease in damping of torsional oscillations in the LSDW phase, which effect was predicted by Overhauser [24]. The minimum in these oscillations occurs at \( \sim 240 \) K, a temperature that is close to the one at which there is a local minimum in \( -\ln(f/f_0) \) as presented in figure 2. Also the results found by Street gave clear evidence that the Young modulus and a logarithmic decrement of longitudinal oscillations are characteristic of the two phases [23]. Finally, as illustrated in figure 3, the width of the Mössbauer spectra measured at half-maximum, which can be regarded as the average amplitude of the SDWs, exhibits two anomalies: one at \( T \approx 145 \) K, below which the increase of the width is linear, and another one at \( T \approx 240 \) K, where the width has a local maximum. Similar behavior was reported previously [25, 26]. The two temperatures coincide very well with those at which the \( f \) factor shows anomalies. All these arguments and observations support our supposition that the anomalous dynamics of Fe atoms embedded in a chromium lattice might be related with the underlying SDWs. However, they do not explain why the dynamics below \( \sim 145 \) K is harmonic and above \( \sim 145 \) K it is not. On the other hand, against a direct relationship between the observed dynamics and the SDWs, the following arguments can be given. First of all, as revealed in this study, the coupling between the probe Fe atoms and the lattice, hence SDWs, is extremely weak, so the probability that the dynamics of the former reflects that of the latter is rather low. Second, the characteristic temperatures found in the present study, i.e. \( \sim 145 \) K, as the border between the harmonic and anharmonic behavior, and \( \sim 240 \) K as the boundary between two anharmonic regions, have no direct
correspondence in the SDWs themselves, for which only one characteristic temperature, i.e. \(~123\ \text{K}\), exists and it marks the transition between LSDW and TSDW phases. Third, the temperature of \(~145\ \text{K}\), which indicates the transition between the harmonic and anharmonic behavior, is close to the Kondo temperature for the Cr–Fe system [27], an effect which has nothing to do with the SDWs. In these circumstances one can only hope that the results presented in this paper will challenge theoreticians to carry out calculations that will shed more light on the dynamics of Fe impurity atoms in chromium.

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