Vol. 91 (1997) ACTA PHYSICA POLONICA A No. 6

# INFLUENCE OF QUADRUPOLE INTERACTION ON $^{57}$Fe MÖSSBAUER SPECTRA FOR SAMPLES WITH CHARGE- AND SPIN-DENSITY WAVES

J. CIEŚLAK AND S.M. DUBIEL*

Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy (AGH)
Al. Mickiewicza 30, 30-059 Kraków, Poland

*(Received January 13, 1997; in final form March 7, 1997)*

The influence of the quadrupole interaction on the shape of $^{57}$Fe Mössbauer spectra expected for samples with charge-density waves and/or spin-density waves is investigated. It is shown, by model calculations, that both for the commensurate and for incommensurate charge-density waves and/or spin-density waves the shape of $^{57}$Fe Mössbauer spectra is sensitive to the value, and for asymmetric spectra, to the sign of quadrupole interaction. This necessitates an inclusion of quadrupole interaction when analyzing the spectra recorded on samples exhibiting charge-density waves and/or spin-density waves, and having a symmetry lower than cubic.

PACS numbers: 75.30.Fv, 75.50.Ee, 76.80.+y

## 1. Introduction

Among modulated electric and spin structures, those whose space modulation can be described by the harmonic function form a special class of systems, and are called charge-density waves (CDW's) and spin-density waves (SDW's), respectively. There are many such systems, in which either pure CDW's or concomitant SDW's have been revealed to exist [1, 2]. The wave vector, $Q$, associated with the CDW or SDW, has the following general relation to the lattice constant, $a$:

$$Q = 2\pi\frac{(1-\epsilon)}{a}, \tag{1}$$

where $\epsilon$ is the commensurability parameter. The wavelength associated with $Q$, $\Lambda_{\mathrm{f}}$ is defined as follows:

$$\Lambda_{\mathrm{f}} = \frac{2\pi}{Q}, \tag{2}$$

*Corresponding author.

which, in view of Eq. (1), can be expressed as

$$\Lambda_{\mathrm{f}} = \frac{a}{(1-\epsilon)}. \tag{3}$$

It follows from Eq. (3) that $\Lambda_{\mathrm{f}} \geq a$. Another measure of the periodicity of the modulation length, $\Lambda_{\mathrm{a}}$, defined by

$$\Lambda_{\mathrm{a}} = \frac{a}{\epsilon} \tag{4}$$

is more pertinent for the present considerations, as by means of the Mössbauer spectroscopy one "sees" the CDW or/and the SDW through probe nuclei sitting on the lattice sites. Based on the two types of the periodicities, i.e. $\Lambda_{\mathrm{f}}$ and $\Lambda_{\mathrm{a}}$, two types of the commensurability can be introduced.

1. If $\epsilon = 0$, $\Lambda_{\mathrm{f}} = a$ and $\Lambda_{\mathrm{a}} = \infty$. All the probe nuclei "see" the same amplitude of the CDW or/and the SDW, and consequently, no effects characteristic of the charge- or/and the spin-density waves will be seen in the Mössbauer spectra.
2. If $\epsilon = 1/n$ and $\Lambda_{\mathrm{a}} = na$ ($n$ being an integer), the probe nuclei will experience a finite number of various amplitudes of the CDW or/and SDW, and, as a result of this, the Mössbauer spectra will show features characteristic of the harmonic modulation.

In both (1) and (2) cases the structure is called commensurate (C).

If $\epsilon \neq 0$ nor $1/n$, the related structure is incommensurate (I) with the lattice. In this case $\Lambda_{\mathrm{a}} \neq na$ and the probe nuclei will experience an infinite number of various amplitudes of the CDW or/and the SDW. CDW's and SDW's can be expressed in terms of higher-order harmonics

$$\mathrm{CDW} = I_0 + \sum_{k=1}^{\infty} I_{2k} \sin(2k\alpha + \delta_{\mathrm{c}}), \tag{5}$$

$$\mathrm{SDW} = \sum_{k=0}^{\infty} H_{2k+1} \sin[(2k+1)\alpha + \delta_{\mathrm{s}}], \tag{6}$$

where $I_0$ is the average charge-density, $I_{2k}$ is the amplitude of the $k$-th order harmonic of the CDW, $\alpha = Qr$ ($r$ being the position vector) and $\delta_{\mathrm{c}}$ is the phase shift between the CDW and the lattice, $H_{2k+1}$ is the $(2k+1)$-th order harmonic of the SDW and $\delta_{\mathrm{s}}$ is the phase shift between the SDW and the lattice. A special procedure for a numerical simulation and/or analysis of the Mössbauer spectra in terms of the harmonics of the CDW or/and the SDW has been developed and described in detail elsewhere [3]. Based on it, the influence of various parameters characteristic of a pure SDW [4], a pure CDW [5] and concomitant CDW and SDW [3] on the shape of Mössbauer spectra and related histograms of charge- and spin-density distributions were studied. As the procedure was originally used to study the CDW and the SDW of chromium, the quadrupole interaction was not taken into account in the previous calculations, in which the spectra were modelled for the $^{119}$Sn isotope, the most successful probe nucleus as far as the SDW and the CDW of chromium is concerned. In order to be able to apply the procedure for the spectra recorded on samples with CDW's or/and SDW's, but with a symmetry lower than cubic, we have extended the procedure by including into the Hamiltonian describing the hyperfine interactions the quadrupole interaction (QS). For the present case we will consider only the simplest case, i.e. such when the electric field gradient (efg) has an axial symmetry. Hence, the eigenvalues of the Hamiltonian describing the QS can be expressed as [6]:

$$E_Q = e^2 q Q_\mathrm{m}[3I_z^2 - I(I+1)]/4I(2I-1), \tag{7}$$

where $e$ is the charge of the proton, $Q_\mathrm{m}$ is the nuclear quadrupole moment, $I$ is the nuclear spin quantum number, $eq$ is the maximum value of the efg and $I_z$ is the $z$-component of $I$. For the $^{57}$Fe isotope, which will be considered here, the resulting spectrum is a so-called quadrupole doublet, with the line splitting, $\Delta E_Q$ given by

$$\Delta E_Q = e^2 q Q_\mathrm{m}/2. \tag{8}$$

There are many systems known, with a lower-than-cubic symmetry, which exhibit the CDW [1]. Chalcogenides are the best known among them. However, only few of them were investigated by means of the Mössbauer spectroscopy, and even less using the effect at $^{57}$Fe nuclei. To the latter case belong the studies on monoclinic Fe-doped $TaS_3$ and $TaSe_3$ [7, 8], as well as on trigonal $FeNb_3S_{10}$ [9]. Although the spectra were analyzed in terms of methods in which the harmonical modulation of the electronic structure had not been included a priori, the authors managed to demonstrate CDW-induced changes in the electric field gradient and isomer shift.

Concerning the non-cubic systems with the SDW, we are aware of only one, viz. the eskebornite ($CuFe_2Se_2$) [10].

## 2. Calculation of the spectra

The spectra were calculated using the procedure described in detail elsewhere [3–5]. Its basic features are as follows:

- for a chosen number of higher-order harmonics of the CDW (or the SDW) the resultant shape of the wave is determined for $0° \leq \alpha \leq 360°$ ($0° \leq \alpha \leq 180°$, for the SDW).
- the range of $[0°, 360°]$ ($[0°, 180°]$ for the SDW) is next divided into $L$ equidistant intervals, and for each of them a doublet (a sextet for the SDW) with Lorentzian-shaped lines is constructed with the isomer shift proportional to the amplitude of the CDW in a given interval, and, for the sextet, with the splitting proportional to the amplitude of the SDW in that interval.

In the following calculations it was also assumed that the full width of all lines was the same, and equal to 0.30 mm/s, and, for the sextets, the relative amplitudes of their lines were like 3:2:1.

### *2.1. Commensurate structures, $\Lambda_\mathrm{a} = na$*

#### *2.1.1. Pure CCDW's*

The influence of the value and the sign of $\Delta E_Q$ on the shape of $^{57}$Fe Mössbauer spectra will be illustrated for the CCDW's with the periodicities $\Lambda_\mathrm{a}$ ranging from $2a$ to $5a$. For such periodicities the actual shape of the spectrum is very sensitive to the $n$-value [5]. Two cases will be here considered: (a) $\delta_c = 0°$ i.e. the sinusoidal modulation, and (b) $\delta_c = 90°$ i.e. the cosinusoidal modulation of the

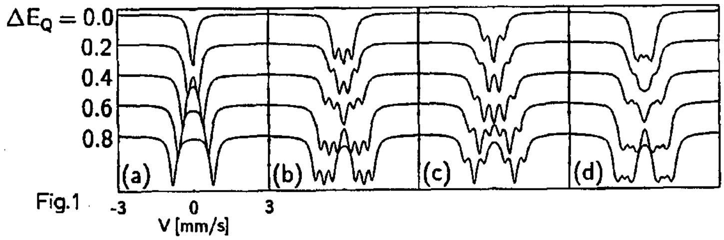



Fig.1

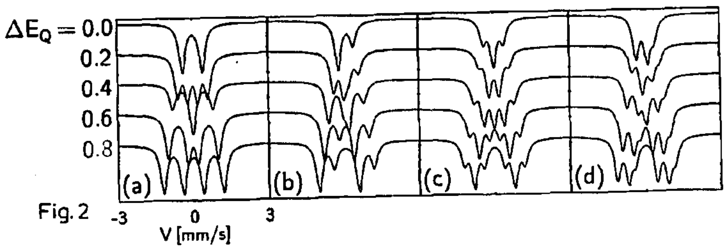



Fig. 2

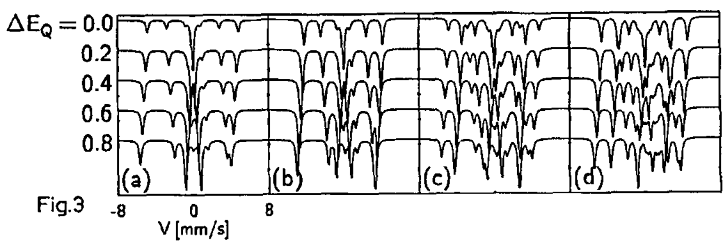



Fig.3

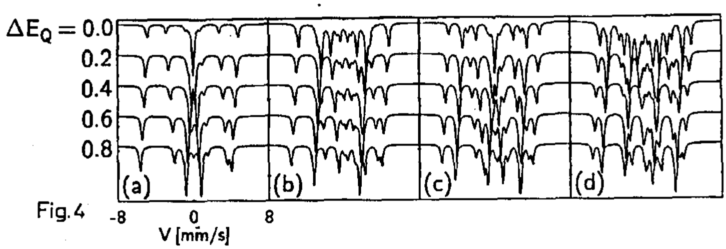



Fig. 4

Fig. 1. $^{57}$Fe Mössbauer spectra calculated for the commensurate CDW, CCDW $= 0.4 \sin 2\alpha$, with the values of $\Delta E_Q$ ranging from 0.0 (top) to 0.8 mm/s (bottom) with the step of 0.2, for (a) $n = 2$, (b) $n = 3$, (c) $n = 4$ and (d) $n = 5$.

Fig. 2. The same as in Fig. 1 but for CCDW $= 0.4 \cos 2\alpha$ ($\delta_c = 90°$).

Fig. 3 $^{57}$Fe Mössbauer spectra calculated for the commensurate sinusoidally modulated SDW, CSDW $= 300 \sin \alpha$ with $\Delta E_Q$ ranging from 0.0 (top) to 0.8 mm/s (bottom) and the step of 0.2, for (a) $n = 2$, (b) $n = 3$, (c) $n = 4$ and (d) $n = 5$.

Fig. 4. The same as in Fig. 3 but for the cosinusoidal modulation of the CSDW ($\delta_s = 90°$).

CCDW. A selection of the spectra calculated for the case (a) CCDW $= 0.4 \sin\alpha$ and $\Delta E_Q$ ranging from 0.0 to 0.9 mm/s is presented in Fig. 1a through 1d. As can be seen for all periodicities shown the $\Delta E_Q$-value strongly affects the actual shape of the spectrum which is symmetric. The influence is especially effective for $\Delta E_Q \leq 0.6$ mm/s. For larger values of $\Delta E_Q$, there is a saturation effect as far as the shape of the spectra is concerned, but the splitting continues to increase. Because of the symmetry of the spectra, they are not sensitive to the sign of $\Delta E_Q$. The case (b) will be illustrated for CCDW $= 0.4 \cos\alpha$. A set of calculated spectra is shown in Fig. 2a through 2d. The main difference here in comparison with the spectra shown in Fig. 1 is the fact that spectra for the odd value of $n$ are asymmetric. Consequently, for such periodicities it is possible to determine the sign of $\Delta E_Q$, as its change manifests itself in the change of the symmetry of the spectra (they have a mirror symmetry with respect to the sign of $\Delta E_Q$). Both symmetric and asymmetric spectra are sensitive to the value of $\Delta E_Q$, especially in the range up to 0.6 mm/s.

*2.1.2. Pure CSDW's*

The influence of $\Delta E_Q$ will be presented here for the fundamental CSDW with the amplitude of 300 kOe and (a) $\delta_s = 0°$ i.e. with the sinusoidal modulation, and (b) $\delta_s = 90°$ i.e. with the cosinusoidal modulation. The spectra calculated for CSDW $= 300 \sin\alpha$, and various $n$ shown, are displayed in Fig. 3a through 3d. One can easily notice that their shape depends on the $n$-value, and for the given $n$ it depends on $\Delta E_Q$. However, contrary to the case of the pure CDW's, the influence of the $\Delta E_Q$-values seems here to be rather isotropic in the sense, both small, medium and large value of $\Delta E_Q$ have a similar effect on the shape of the spectrum. The spectra shown in Fig. 4 for the case (b), i.e. CSDW $= 300 \cos\alpha$, have different shape than those presented in Fig. 3 which proves that the spectrum is sensitive both to the value of the phase shift, $\delta_s$, and to the value of the quadrupole splitting $\Delta E_Q$. As the spectra displayed both in Fig. 3 and Fig. 4 are asymmetric, the reversal of the $\Delta E_Q$ sign leads to the reversal of the symmetry of the spectra, allowing thereby its determination.

*2.1.3. Concomitant CCDW and CSDW*

It is believed that via spin–phonon interactions SDW's are always accompanied by the concomitant CDW's [11]. Such a case will be considered below for the fundamental CSDW with the amplitude of 300 kOe and the concomitant CCDW with the amplitude of 0.2 mm/s, both having the sinusoidal modulation, i.e. the relative phase shift $\delta = 0°$ (CSDW $= 300 \sin\alpha$ and CCDW $= 0.2 \sin 2\alpha$). The spectra obtained for this case are presented in Fig. 5a through 5d for various periodicities, and for $\Delta E_Q$ ranging from 0.0 to 0.8 mm/s with the step of 0.2. The spectra provide a clear evidence that their shape, which is characteristic, as before, of the $n$-value, sensitively depends on the $\Delta E_Q$-value in the whole range studied. The asymmetry of the spectra makes it possible to determine the sign of $\Delta E_Q$. Following previous calculations [3], the shape of the spectra for concomitant SDW's and CDW's depends on the relative phase shift, $\delta$, between the SDW and the CDW. Therefore, one expects such dependence to exist

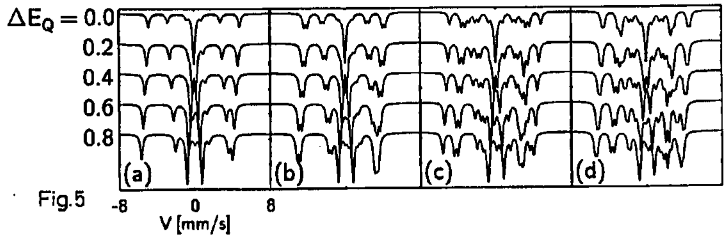


Fig.5

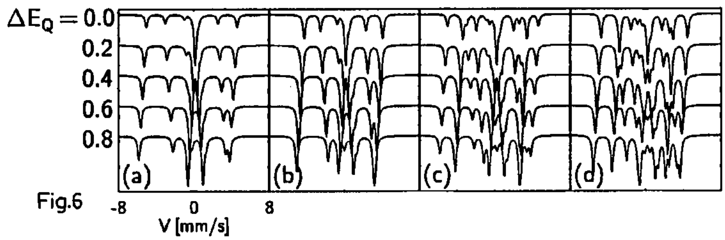


Fig.6

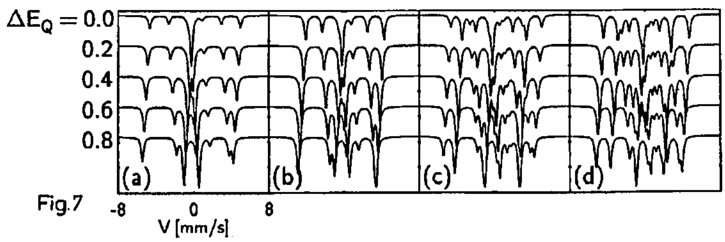


Fig.7

Fig. 5. $^{57}$Fe Mössbauer spectra calculated for the commensurate SDW, CSDW = $300 \sin\alpha$ and the concomitant commensurate CDW, CCDW = $0.2 \sin 2\alpha$, i.e. $\delta = 0°$, as a function of $\Delta E_Q$ ranging from 0.0 (top) to 0.8 mm/s (bottom) and the step of 0.2, for (a) $n = 2$, (b) $n = 3$, (c) $n = 4$ and (d) $n = 5$.
Fig. 6. The same as Fig. 5 but for the cosinusoidal modulation ($\delta = 90°$).
Fig. 7. The same as Fig. 5 but for $\delta = -90°$.

also in the presence of the quadrupole interaction. To show this, the spectra for CSDW = $300 \sin\alpha$ and CCDW = $0.2 \sin(2\alpha + 90°)$ i.e. for the cosinusoidal modulation were simulated and they are shown in Fig. 6a through 6d, proving that the expectation was correct. To reveal whether the spectra are sensitive to the sign of $\delta$, a set of the spectra for CSDW = $300 \sin\alpha$ and CCDW = $0.2 \sin(2\alpha - 90°)$ was simulated. They can be seen in Fig. 7a through 7d and give a clear evidence that the sign of $\Delta E_Q$ is also important in this case.

### *2.2. Incommensurate structure, $\Lambda_a \neq na$*

#### *2.2.1. Pure ICDW*

To illustrate the influence of the quadrupole interaction on the shape of the Mössbauer spectra the ICDW = $I_2 \sin 2\alpha$ is considered, and the spectra are simulated for $\Delta E_Q$ ranging from 0.0 to 0.8 mm/s. Those obtained for (a) $I_2 = 0.0$ mm/s,

(b) $I_2 = 0.2$ mm/s, (c) $I_2 = 0.4$ mm/s and (d) $I_2 = 0.6$ mm/s are presented in Fig. 8a through 8d, respectively. It is evident that $\Delta E_Q$ has a strong effect on the actual shape of the spectrum. However, similarly to the case of the pure CCDW, the effect shows a saturating behaviour with the increase in the $\Delta E_Q$-value, as far as the shape of the spectra is concerned. The spectra are symmetric, so they are insensitive to the sign of $\Delta E_Q$.

*2.2.2. Pure ISDW*

First, the fundamental ISDW with the amplitude $H_1$ and the phase shift $\delta_s = 0°$ i.e. ISDW = $\mathrm{H}_1 \sin\alpha$ will be considered. To show the influence of $H_1$ on the shape of the spectra in the presence of the quadrupole interaction, the spectra with various values of $H_1$ were simulated for $\Delta E_Q$ ranging between 0.0 and 0.8 mm/s. They can be seen in Fig. 9a for $H_1 = 300$ kOe and in Fig. 9b for $H_1 = 400$ kOe. Their shape, for both $H_1$-values, is sensitive to the $\Delta E_Q$-value in its whole range studied. In Fig. 9c and Fig. 9d the spectra simulated for ISDW $= 300\sin\alpha + 50\sin 3\alpha$ and for ISDW $= 300\sin\alpha - 50\sin 3\alpha$ are presented, respectively. They prove that also in such a case the shape of the spectra depends on the $\Delta E_Q$-value. As all the spectra shown in Fig. 9 are asymmetric, they reverse their asymmetry by reversing the sign of $\Delta E_Q$, allowing thereby the determination of the sign of $\Delta E_Q$.

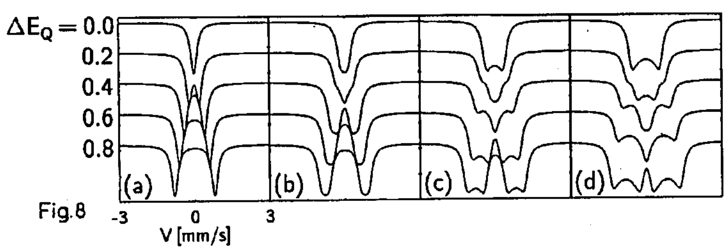



Fig.8

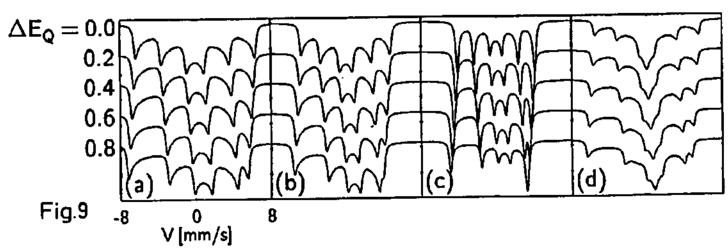


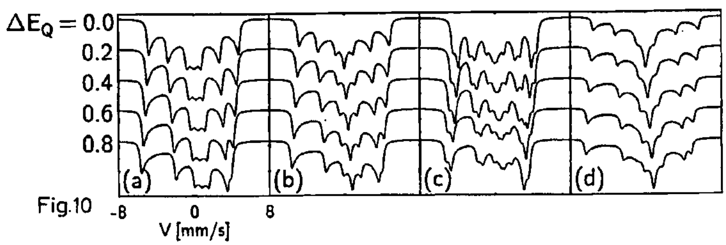

Fig.9

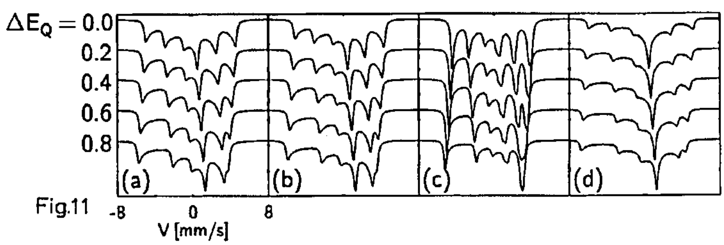
Fig. 8. $^{57}$Fe Mössbauer spectra simulated for the incommensurate CDW and $\delta_c = 0°$, ICDW $= \mathrm{I}_2 \sin 2\alpha$, and various $\Delta E_Q$ values ranging between 0.0 (top) and 0.8 mm/s (bottom) with the step of 0.2 as a function of the ICDW amplitude $I_2$ equal to (a) 0.0 mm/s, (b) 0.2 mm/s, (c) 0.4 mm/s and (d) 0.6 mm/s.

Fig. 9. $^{57}$Fe Mössbauer spectra for a pure incommensurate SDW and $\delta_s = 0°$ in the presence of the quadrupole interaction with $\Delta E_Q$ ranging between 0.0 (top) and 0.8 mm/s (bottom) and the step of 0.2 for (a) ISDW $= 300\sin\alpha$, (b) ISDW $= 400\sin\alpha$, (c) ISDW $= 300\sin\alpha + 50\sin 3\alpha$, and (d) ISDW $= 300\sin\alpha - 50\sin 3\alpha$.

*2.2.3. Concomitant ICDW and ISDW*

Spectra displayed in Fig. 10 illustrate the influence of the quadrupole interaction on the shape of the spectra for the following particular cases: (a) ISDW $= 300\sin\alpha$ and ICDW $= 0.2\sin 2\alpha$, (b) ISDW $= 300\sin\alpha$ and ICDW $= 0.4\sin 2\alpha$, (c) ISDW $= 300\sin\alpha + 50\sin 3\alpha$ and ICDW $= 0.4\sin 2\alpha$, and (d) ISDW $= 300\sin\alpha - 50\sin 3\alpha$ and ICDW $= 0.4\sin 2\alpha$. Meaningful changes in the spectra can be observed for all the values of $\Delta E_Q$ considered. The asymmetry of the spectra provides information on the sign of $\Delta E_Q$. The spectra shown in Figs. 11 and 12 give evidence that the value of the phase shift, $\delta$, and its sign have also profound influence on the shape of the spectra in the presence of the quadrupole interaction.



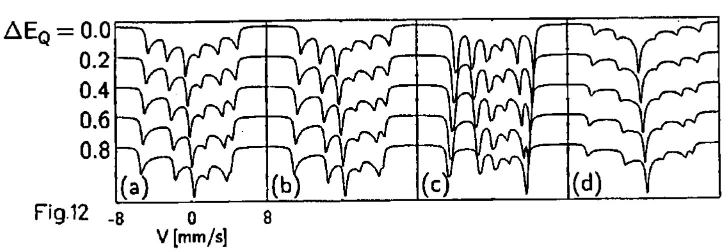




Fig. 10. $^{57}$Fe Mössbauer spectra calculated for ISDW's and concomitant ICDW's for various values of $\Delta E_Q$ ranging between 0.0 (top) and 0.8 mm/s (bottom) with the step of 0.2. (a) ISDW $= 300\sin\alpha$ and ICDW $= 0.2\sin 2\alpha$, (b) ISDW $= 300\sin\alpha$ and ICDW $= 0.4\sin 2\alpha$, (c) ISDW $= 300\sin\alpha + 50\sin 3\alpha$ and ICDW $= 0.4\sin 2\alpha$, and (d) ISDW $= 300\sin\alpha - 50\sin 3\alpha$ and ICDW $= 0.4\sin 2\alpha$.

Fig. 11. The same as in Fig. 10 but with the phase shift between the ISDW and ICDW $\delta = 90°$.

Fig. 12. The same as in Fig. 10 but with the phase shift between the ISDW and ICDW $\delta = -90°$.

## 3. Summary and conclusions

Using the model calculations it was shown that the amplitude of the quadrupole interaction for the electric field gradient with axial symmetry has a strong influence on the shape of the Mössbauer spectra in case of pure and/or mixed charge- and spin-density waves. In certain cases, viz. when the spectra are asymmetric, they are also sensitive to the sign of QS. In view of these results it is evident that this interaction has to be taken into account when analyzing spectra recorded on samples with harmonically modulated electric and/or spin structures, and having a symmetry lower than cubic.

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