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APPLICATION OF ¹¹⁹Sn MÖSSBAUER-EFFECT SPECTROSCOPY IN THE INVESTIGATION OF SPIN-DENSITY-WAVES IN CHROMIUM

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Application of ¹¹⁹Sn Mössbauer-effect spectroscopy in an investigation of spin-density-waves in chromium in terms of model calculations as well as of measurements on real samples is presented.

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1. Introduction

A great interest in chromium stems from (a) its technological importance and (b) its fascinating magnetic properties constituted by the so-called spin-density-waves (SDW).

This paper is devoted to the latter subject, and more precisely, to the topic of what one can learn about SDW using ¹¹⁹Sn Mössbauer-offect spectroscopy (MES) for that purpose. The paper is organized as follows: In Sec. 2 the properties of SDW such as: (a) magnetic structure, (b) domain structure, (c) spin-flip transition, (d) higher-order harmonics are presented. In Sec. 3 the influence of different SDWparameters, such as the sign and the magnitude of higher-order harmonics in case of incommensurate SDW (ISDW), the wave-length and the mode of the wave-modulation, for the commensurate SDW (CSDW), is outlined. Finally, in Sec. 4, recent experimental results concerning the influence of foreign atoms (Sn, V, Fe and Mn), of the strain and of the grain size on ISDW is presented and discussed.

2. Antiferromagnetism of chromium

2.1. Magnetic structure

Metallic chromium is one of the best known examples of an antiferromagnet. It is, however, not a simple system, since the magnitude of the magnetic moment per Cr atom μ is modulated in space in the following manner [1]:

$$\mu = \mu_0 n \sin(\mathbf{Q} \cdot \mathbf{r}),$$

(2.1)

where $\mu_0 = 0.59 \ \mu_B$, *n* is the unit polarization vector, *Q* is the wave vector of the magnetic modulation and *r* is the position vector.

Equation (2.1) gives rise to say that the antiferromagnetism of chromium is constituted by SDW. Both d- and s-like itinerant electrons contribute to SDW. The polarization direction of SDW n depends on temperature T. In this respect one can distinguish two ranges:

(a) $T_{\rm sf} \leq T \leq T_{\rm N}$, where $T_{\rm N} \approx 312$ K is the Neel temperature and $T_{\rm sf} \approx 123$ K is the so-called spin-flip temperature. In this range the polarization of SDW is perpendicular, i.e. $Q \cdot n = 0$ and this state of SDW is called the transverse SDW state (TSDW). It is also called AF₁.

(b) $T \leq T_{sf}$. In this range the polarization of SDW is paralell, i.e. $Q \cdot n = 1$. SDWs in this state are called the longitudinal SDW (LSDW) and the range of their existence is also labelled as AF₂.

It has been also found that SDW of chromium are incommensurate with the underlying lattice periodicity. This means that

 $Q \neq 2\pi/a, \tag{2.2}$

where a is the lattice constant.

In order to describe a departure from the commensurability, one introduces a parameter δ such that

$$Q = 2\pi (1 - \delta)/a. \tag{2.3}$$

It was experimentally found that δ is a smooth function of T and the periodocity of SDW $\Lambda = a/\delta$, which is an adequate parameter for the present considerations, lies between $\approx 20 a$ at LIIT and $\approx 28 a$ at RT [1, 2]. Strictly speaking, the incommensurate structure (ICS) exists only for $\Lambda \neq ma$ (*m* being the natural nimber) and for $\Lambda = ma$ the structure is commensurate (CS).

2.2. Domain structure

Any SDW can be characterized by its wave vector Q_i and the unit polarization vector n_j , where in case of chromium i, j = 1, 2, 3. A volume, throughout which there is only one SDW, is called a domain. A single crystal of chromium in its AF₁ (TSDW) state consists of up to six different domains $(Q_i, n_j)_{i\neq j}$ (SDWs propagate paralell to the main crystallografic directions). In AF₂ (LSDW) state three different domains can coexist. Because of this threefold orientational degeneracy of Q, such a state is called 3-Q state.

An application of an external magnetic field B_0 can change this picture. If B_0 is strong enough, a state can be produced in which only domains with $n \perp B_0$ survive. Consequently, in AF₁ these are domains with $Q \parallel B_0$, e.g. if $B_0 \parallel$ [100] these are the following domains: (Q_1, n_2) and (Q_1, n_3) . This state, which is characterized by a single Q-value, is called then 1-Q or a single-Q. In AF₂ domains with $Q \perp B_0$ survive. For instance, if $B_0 \parallel$ [100] these are the following domains: (Q_2, n_2) and (Q_3, n_3) . As these domains are characterized by two different values of Q, this state is called 2-Q.

According to Köbler and Dubiel [3], the critical values of B_0 to produce 1-Q and 2-Q states are equal to ≈ 1.6 T and ≈ 4.5 T, respectively.

2.3. Spin-flip transition

At $T \approx 123$ K SDWs change their polarization. This phenomenon known as the spin-flip transition has attracted a remarkable interest and it was successfully studied by numerous techniques [4] like: neutron scattering (1961), torque measurements (1964), magnetic susceptibility (1966), thermal expansion and magnetostriction (1969), Young's modulus (1971), perturbed angular correlations (1978), ultrasonic attenuation (1981) and ¹¹⁹Sn Mössbauer-effect spectroscopy (1984). The latter results gave evidence [5] that the transition is more complex in its nature than it was previously thought: firstly, because it exhibits precursor effects extending over a range of several degrees K, and secondly, because it shows a rather broad hysteresis.

2.4. Higher-order harmonics

2.4.1. Second-order term

X-ray [6] and neutron diffraction [7] experiments revealed weak satellite reflections at the wave vector $q = \tau \pm 2Q$, with τ being the reciprocal lattice vector of the bcc chromium. The relative contribution of the second-order harmonic of SDW as being equal to 1.6 or 2.6×10^{-3} could be determined from these measurements, respectively.

2.4.2. Third-order term

First evidence of the existence of the third-order harmonic of SDW was found by Pynn and co-authors [7] from their neutron diffraction experiment. Its polarization was identical with that of the fundamental SDW and its relative contribution was determined to be equal to $1.65(5) \times 10^{-2}$ at 200 K, i.e. one order of magnitude larger than the contribution of the second-order harmonic. The existence of the third-order term deforms the resulting SDW in such a way that their shape is not purely sinusoidal but it is slightly rectangular-like.

Recent ¹¹⁹Sn Mössbauer-effect measurements by Dubiel and Le Caër [8] on a (110) face of a single-crystal sample of Cr doped with 0.18 at% ¹¹⁹Sn demonstrated that also by this method one is able to detect the third-order term in SDW. Using the sinusoidal approach the authors obtained the value of $2.5(8) \times 10^{-2}$, whereas an alternative cosinusoidal approach to the analysis of the spectrum provides the value of 1.8×10^{-2} .

3. Influence of SDW parameters on ¹¹⁹Sn Mössbauer spectra

For Sn probe atoms randomly distributed in the chromium matrix, the hyperfine field (hf) H can be written as follows [9]:

$$H = H_1 \sin(Q \cdot r), \tag{3.1}$$

or

$$H = H_1 \cos(\mathbf{Q} \cdot \mathbf{r}) \tag{3.2}$$

where

$$Q = i \cdot Q_1 + j \cdot Q_2 + k \cdot Q_3, \tag{3.3}$$

$$= (im + jn + kl)a \tag{3.4}$$

or

r

$$\mathbf{r} = [\mathbf{i}(m+1/2) + \mathbf{j}(n+1/2) + \mathbf{k}(l+1/2)]a$$
(3.5)

and $-\infty \leq m, n, l \leq +\infty$.

Let us assume $Q \parallel k$. Then, only the Q_3 -component differs from zero and we can define it as $Q = 2\pi(1-\delta)/a$. From Eqs. (3.1) through (3.5) it follows that the following two contributions, for cos or sin version, to H exist:

$$H_a = H_1 \cos(2\pi\delta p), \qquad H_b = -H_1 \cos(2\pi\delta p + \pi\delta)$$
(3.6)

or

$$H_a = H_1 \sin(2\pi\delta p), \qquad H_b = H_1 \sin(2\pi\delta + \pi\delta), \tag{3.7}$$

where $-\infty \le p \le +\infty$. As expected, if $\delta = 0$ (the case of a normal antiferromagnet) only two fields, viz. $H = \pm H_1$ are obtained, while for $\delta \ne 0$, two cases may be distinguished depending on the values of $\Lambda = a/\delta$, i.e. the periodicity of SDW:

(a) for $\Lambda = ma$ only a finite number of inequivalent Mössbauer sites, hence subspectra, exists; and

(b) for $\Lambda \neq ma$ an infinite number of Mössbauer sites is expected.

Case (a) corresponds to a commensurate structure (CS) and case (b) represents an incommensurate structure (ICS).

3.1. ICS — first-order term

In this case the argument of the cos or the sin term in (3.6) and (3.7) is uniformly distributed within the range of $[0, 2\pi]$. The corresponding hf field distribution (HFD) has the following form [9]:

$$p(H) = 2/[\pi(H_1^2 - H^2)]^{1/2}.$$
(3.8)

Such a distribution, which is illustrated in Fig. 1a, gives rise to a broad Mössbauer spectrum, which is presented in Fig. 1b. A characteristic feature of this IIFD-histogram is the existence of the peak situated at $H = H_1$.

3.2. Case
$$\Lambda = ma$$
 (CS)

In order to illustrate how the value of the periodicity of CSDW influences the shape of the ¹¹⁹Sn Mössbauer spectra, Fig. 2 presents a selection of them obtained for various A-values. The spectra represented by solid lines stay for the sin-like modulation of SDW while those marked by dotted lines show the cos-like modulated SDW. The following characteristic feature can easily be noticed:

(a) the actual shape of a spectrum depends sensitively on the value of Λ and particulary for its smaller values;

(b) for $\Lambda = 2ma$ cos- and sin-like spectra are identical;

(c) with increasing A-value cos- and sin-like spectra get similar to each other and for $A \ge 15a$ they are practically the same and they cannot be distinguished from the spectrum characteristic of the ICS case (see Fig. 1b).

As for chromium the smallest value of $\Lambda \approx 20a$, one would not be able to distinguish between the ICS and the CS structure from the Mössbauer spectra. For



Fig. 1. HFD-histogram as obtained from Eq. (3.8) for pure sinusoidal SDW (a) and the corresponding ¹¹⁹Sn Mössbauer spectrum (b).



Fig. 2. ¹¹⁹Sn Mössbauer spectra calculated for $\Lambda = ma$ for various values of m. The solid-line spectra stay for the sinusoidally modulated SDW and the dotted-line spectra for the cosinusoidally modulated SDW.

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 $\Lambda = 28a$ the influence of the intensity of the 2nd and the 5th lines, $I_{2,5}$ on the shape of the spectrum is also presented in Fig. 2, in order to illustrate the influence of the TSDW-LSDW transition in a 1-Q state on the shape of the spectrum (spectrum labelled with a28 represents the case of $I_{2,5} = 0$ and that labelled with b28 is for the case of $I_{2,5} = 4$).

3.3. ICS case — higher-order harmonics

3.3.1. Second-order term

If one assumes that the second-order harmonic of SDW exists, then the hf field can be written as follows:

$$H = H_1 \sin \alpha + H_2 \sin 2\alpha. \tag{3.9}$$

For $H \ge 0$ and $\alpha = [0, \pi]$, the average hf field, \overline{H} is given by the following expression:

$$\overline{H} = 2H_1/\pi \tag{3.10}$$

and the standard deviation σ by

$$\sigma = \left[(H_1^2 + H_2^2)/2 - 4H_1^2/\pi^2 \right]^{1/2}.$$
(3.11)

It is clear from Eq. (3.10) that \overline{H} does not depend on H_2 , while σ exhibits some weak dependence only. For example, in case of $H = 55 \sin \alpha + 11 \sin 2\alpha$, $\sigma = 18.6$ kOe instead of 16.9 kOe, as expected for the purely sinusoidal SDW.

3.3.2. Third-order term

If one restricts itself to the fundamental SDW and to the 3rd-order term, the resulting expression for H reads as follows:

$$H = H_1 \sin \alpha + H_3 \sin 3\alpha. \tag{3.12}$$

The corresponding HFD-curve has the following form [9]:

$$p(H) = 2\sum \left[\sqrt{(1-x_i^2)}|12H_3x_i^2 - H_1 - 3H_3|\right]^{1/2}/\pi.$$
(3.13)

It follows from Eq. (3.13) that there are two discontinuities in p(H), viz. at $x_i = 1$ and at $x_i = [|H_1 + 3H_3|/12|H_3|]^{1/2}$. In other words, the presence of the third-order harmonic manifests itself through additional peak in the HFD.

As shown in Fig. 3, the relative intensity and the distance between the two peaks depend on the sign of H_3 and its ratio to H_1 . In particulary, it is easy to see that for:

(a) $R = H_3/H_1 \leq 0$, $H_{\text{max}} \geq H_1$ and it linearly increases with the increase in the ratio R;

(b) $H_3/H_1 \ge 0$, there are two characteristic regions, namely one for $R \le 0.4$, $H_{\max} \le H_1$ reaching a minimum at $R \approx 0.18$ and the other for $R \ge 0.4$, where $H_{\max} \ge H_1$.

Figure 4, on the other hand, displays ¹¹⁹Sn Mössbauer spectra calculated for various negative (a) and positive (b) values of R marked. Here, for $R \leq 0$ one can see a characteristic development of a single-line peak in the central part of spectra whose relative contribution increases with the increasing R-value as well



Fig. 3. The normalized maximum hf field H_{max}/H_1 as a function of the relative contribution of the third-order harmonic $R = H_3/H_1$. H_1 is the amplitude of the fundamental SDW.



Fig. 4. ¹¹⁹Sn Mössbauer spectra calculated for $II = |II_1 \sin \alpha + H_3 \sin 3\alpha|$ for various values of R.

as an increase of the maximum field. For $R \ge 0$, the spectra develop in a more complex way. The most characteristic difference in comparison with the spectra found for $R \le 0$ is a deep instead of the single-line in the centre of the spectra.

The above-presented considerations can be further generalized by an inclusion of other higher-order harmonics [9].

To conclude this Section one can state that ¹¹⁹Sn Mössbauer spectra have turned out to be sensitive both to the sign and to the amplitude of the third-order term, in case of the incommensurate SDW and to the wave-length in case of the commensurate SDW.

4. Influence of foreign atoms, strain and grain size on SDW

A. Experimental results

A.4.1. Influence of foreign atoms

The following foreign atoms have been chosen to study their influence on SDW: Sn, Fe, V and Mn. These particular atoms have been selected for the following reasons: Sn atoms — because they are used as probe nuclei, so their influence on the properties of SDW is of a primary interest and importance; Fe and V atoms because they are known as strongly suppressing SDW and finally Mn atoms because they were revealed to change the character of SDW from an incommensurate to a commensurate state.

 $Cr_{100-y}Sn_y$, $(Cr_{100-x}Fe_x)_{100-y}Sn_y$, $(Cr_{100-x}V_x)_{100-y}Sn_y$ and $(Cr_{100-x}Mn_x)_{100-y}Sn_y$ alloys were prepared by melting appropriate amounts of chromium (4N-purity), iron (4N-purity), vanadium (5N-purity), manganese (3N-purity) and tin (3N-purity), the latter being enriched to ≈ 91 at% in the ¹¹⁹Sn isotope, in an arc furnace under pure argon atmosphere.

The composition of the ingots was analyzed by means of the atom emission spectroscopy (AES). The results obtained are displayed in Table I.

TABLE I

Composition of $(Cr_{100-x}Z_x)_{100-y}Sn_y$ alloys (Z = Fe, V, Mn) as determined by means of the AES analysis with the relative error of ± 2 %.

Sn	Fe		V		Mn	
y	x	y	x	y	x	\boldsymbol{y}
0.07	1.42	0.52	0.64	0.64	0.08	0.27
0.58	2.66	0.42	2.52	0.53	0.18	0.10
0.73	3.29	0.36	5.26	0.57	0.31	0.16
1.18	4.16	0.44			1.08	0.15
	6.00	0.48				
	7.26	0.84				

A.4.1.1. Chromium-tin alloys

RT ¹¹⁸Sn Mössbauer spectra of these alloys are presented in Fig. 5. In all cases, a single-line subspectrum, marked by an arrow, can be seen. It was identified as arising from the probe nuclei in the undissolved β -tin. The shape of the spectra is quite different than that characteristic of the sinusoidally modulated SDW (see Fig. 1b). A possible reason for this difference will be discussed in Sec. 4.2. of this paper.



Fig. 5. RT ¹¹⁹Sn Mössbauer spectra of Cr–Sn alloys. The arrows indicate the position of the subspectrum due to undissolved β -tin and the figures are for the concentration of tin in at%.

Fig. 6. HFD-curves obtained from the spectra shown in Fig. 5 for y = 0.07 (A), y = 0.58 (B), y = 0.73 (C), and y = 1.18 (D).

The spectra were analyzed by means of a mode-lindependent fitting procedure [10] that yielded the corresponding IIFD-curves shown in Fig. 6. They exhibit a complex many-peak structure, instead of one peak as in case of the fundamental SDW (see Fig. 1a), which in general does not depend on the tin concentration in the samples.

A.4.1.2. Chromium-vanadium alloys

RT ¹¹⁹Sn Mössbauer spectra of these alloys are displayed in Fig. 7. According to the phase diagram of the Cr-V system [11], all the three samples studied should be in a paramagnetic phase at this temperature, i.e. their Mössbauer spectra should consist of a single line only. One can, however, see that all three spectra show shoulders on both sides of the dominating single line. Only a fraction of the right-side shoulder, which position is indicated by an arrow, can be accounted for by the line due to undissolved β -tin.

HFD-curves, which were derived from the spectra by the method from Ref. [10] and are presented in Fig. 8, give another picture of a residual magnetic component. Here, three peaks of minute but finite probabilities exist in the range of 10-35 kOe. From neutron diffraction experiments the existence of disordered local spins in the paramagnetic phase of the Cr-V system was revealed with a correlation length of about 30 Å [4]. This could account for the small magnetic splitting presently observed in the Mössbauer spectra of these alloys.



Fig. 7. RT ¹¹⁹Sn Mössbauer spectra of Cr–V alloys. The arrows indicate the position of the subspectrum due to undissolved β -tin. The figures indicate the concentration of vanadium in at%.

Fig. 8. HFD-curves obtained from the spectra shown in Fig. 7: x = 0.64 (A), x = 2.54 (B), and x = 5.25 (C).

A.4.1.3. Chromium-iron alloys

Figure 9 illustrates RT ¹¹⁹Sn Mössbauer spectra of a series of Cr-Fe alloys studied. Their shape is quite similar to that found for the Cr-Sn samples, especially for lower values of iron content. Also here a definite fraction of undissolved Sn atoms exists. The corresponding subspectrum is marked by arrows in Fig. 9.

An expected quenching effect of Fe atoms on SDW can easily be seen from the

HFD-curves, which are presented in Fig. 10. There, the component at $H \approx 80$ kOe gradually disappears with the increasing concentration of iron.

Another interesting feature to be noticed is that according to the magnetic phase diagram of the system [12], all our samples of Cr-Fe should be at RT in a paramagnetic state. The IIFD-curves in Fig. 10 give, however, evidence that the well-defined magnetic components are still there. This feature can be understood in the light of (a) the magnetic phase diagram of the strained chromium [13], which characteristic pertinent feature is an increase in the Néel temperature (as our samples were obtained by filling bulk ingots, they certainly were in a strained states) and (b) locally correlated disordered spins, as already mentioned in A.4.1.2.



Fig. 9. RT ¹¹⁹Sn Mössbauer spectra of Cr-Fe alloys. The arrows indicate the position of the subspectrum due to undissolved β -tin. The figures stay for the concentration of iron in at%.

Fig. 10. HFD-curves obtained from the spectra shown in Fig. 9: x = 1.4 (A), x = 2.7 (B), x = 4.2 (C), and x = 6.0 (D), respectively.

A.4.1.4. Chromium-manganese alloys

¹¹⁹Sn Mössbauer spectra registered at RT for these alloys can be seen in Fig. 11. A contribution of a single-line subspectrum due to undissolved β -tin is marked by arrows.

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Concerning the shape of the spectra, one can easily notice that an increase in Mn content in the Cr matrix brings about significant changes. In particular, the following features change: (a) an intensity of a central single-line subspectrum decreases, (b) a six-line pattern, characteristic of a commensurate structure develops and (c) the maximum splitting increases. These features can also be well seen in the corresponding IIFD-curves in Fig. 12.



Fig. 11. RT ¹¹⁹ Sn Mössbauer spectra of Cr-Mn alloys. The arrows indicate the position of the subspectrum due to undissolved β -tin. The figures stay for the concentration of manganese in at%.

Fig. 12. HFD-curves obtained from the spectra shown in Fig. 11: x = 0.08 (A), x = 0.18 (B), x = 0.31 (C), x = 1.08 (D), respectively.

A.4.2. Influence of strain

A great body of experimental data proves that properties of SDW of chromium depend significantly on strain [4]. Consequently any comparison of results, obtained even with the same experimental method but on samples having different history or prepared in a different way, does not seem to be adequate.

All the Mössbauer spectra which are discussed in Sec. A.4.1. were registered on samples in form of powder obtained by filling as-obtained bulk ingots. Consequently, all the samples were in a strained state.

In order to reveal an influence of the strain on the shape of the Mössbauer spectra, the strain was released in some Cr-Sn and Cr-Mn samples by annealing them for 5h at 800°C and the Möessbauer spectra were registered for those strain-free samples. The spectra were fitted to yield the IIFD-curves, which are displayed elsewhere [14].

A.4.3. Influence of a grain size

Let us start with recalling the shape of the ¹¹⁹Sn Mössbauer spectrum, which one expects for the sinusoidally modulated SDW. Figure 1b shows such a spectrum and the related IIFD-histogram is presented in Fig. 1a. If one compares this spectrum with those presented in Fig. 5 for polycrystalline samples of chromium then a big difference between them can immediatelly be seen. The main dissimilarity can be observed in the central part of the spectra of the latter where a significant single-line subspectrum exists. Such a subspectrum was absent in a spectrum registered on a (110) face of a single-crystal sample of chromium [8], see also Fig. 13. What is the reason for this difference in the shape of the spectra?



Fig. 13. RT ¹¹⁹Sn Mössbauer spectrum measured for a (110) face of a single-crystal chromium.

In order to try to answer this question we notice that the most significant difference between the samples involved is that the former are polycrystalline while the latter was a single-crystal. Consequently, we assume that the difference in the shape of the spectra originates from the difference in the microstructure.

To find more evidence in favour of this assumption, a new polycrystalline sample of Cr–Sn alloy was prepared from a bulk piece of chromium in form of a 100 μ m thick foil. ¹¹⁹Sn probe nuclei were introduced into the Cr matrix by means of a diffusion as described previously [8]. The resultant RT Mössbauer spectrum is shown in Fig. 14. It has the central single-line subspectrum characteristic of

polycrystalline samples, but its overall shape seems to be intermediate between this in Fig. 5 and that in Fig. 13.

In order to increase the size of grains in this sample, it was a subject of recrystalization. Subsequent analysis of the microstructure by means of the electron microscope permitted to estimate the size of grains to lie between 60-200 μ m, which is greater by the factor of two than before the recrystalization and greater by the factor of four than the size of grains in the powder samples.



Fig. 14. RT ¹¹⁹Sn Mössbauer spectrum of a polycrystalline strain-free sample of an $Cr_{99.8}Sn_{0.2}$ alloy in the form of a foil.

Fig. 15. The same as in Fig. 14 but after the recrystalization of the sample.

RT Mössbauer spectrum of the recrystalized sample can be seen in Fig. 15. A significant change of its shape in comparison with that shown in Fig. 14 can easily be recognized, in particular a strong reduction of the central single-line subspectrum.

B. Discussion

B.4.1. The influence of foreign atoms

The results presented in Sec. A.4.1. have given a clear evidence that ¹¹⁹Sn Mössbauer spectra are very sensitive to various foreign atoms studied. It has turned out that the spectra registered for polycrystalline samples are much different and more complex than that characteristic of the fundamental SDW. Consequently, their interpretation is more difficult. As the first approach to the problem, we aim at describing the average changes in SDW caused by the foreign atoms studied. For that purpose we consider the average hf field, \overline{H} . Its value can be obtained by the integration of the IIFD-curves in agreement with the following equation:

$$\overline{H} = \int \mathrm{d}H p(H) H. \tag{4.1}$$

	$Cr_{100-x}Sn_x$				$\operatorname{Cr}_{100-x}\operatorname{Fe}_{x}$					
x	0.07	0.58	0.73	1.18	1.42	2.66	3.29	4.16	6.00	7.26
\overline{H}	36.9	37.3	37.4	40.4	30.2	29.1	27.4	25.2	16.6	11.1
	$\operatorname{Cr}_{100-x}\operatorname{Mn}_{x}$			$\operatorname{Cr}_{100-x}\operatorname{V}_x$						
x	0.08	0.18	0.31	1.08	0.64	2.52	5.26			
\overline{H}	45.9	50.5	59.6	74.3	9.0	8.0	6.9			

Average hf fields \overline{H} in kOe, as obtained for the studied samples from Eq. (4.1).

The \bar{H} -values obtained from Eq. (4.1) for all the samples studied are presented in Table II as a function of the concentration of the foreign atoms studied.

Concerning now the influence of the probe atoms themselves, one can see from Table II that for the first three samples of Cr-Sn, \overline{H} stays practically constant and that for the most concentrated sample its value has increased by about 10%. This proves that Sn atoms have practically no influence on SDW of chromium, hence they constitute ideal probe atoms to study the issue.

The behaviour of Fe and V atoms confirms that these atoms quench SDW, V atoms being much more effective. It is perhaps interesting to notice at this point that the decrease in \overline{H} for the Cr-Fe alloys does not follow the behaviour of the average magnetic moment of the system [12] which remains constant up to about 2 at% Fe and then it exhibits a step-like increase correlated with the transition from the incommensurate to the commensurate phase. The difference may results from several factors that differ the present experiment with the one described in [12] and in particular, from (a) the temperature of measurements and (b) the state of samples with respect to the strain. One should also remember that the hf field and the magnetic moment are not always proportional to each other, so their behaviour as a function of a certain parameter must not necessarily be the same. In any case, it would be interesting to carry out Mössbauer-effect measurements at low T.

Finally, concerning the influence of Mn atoms, one can see from Table II that the \overline{H} -value steeply increases with the increase in Mn content. This means that Mn atoms not only change the character of SDW of chromium, which was obvious from the change of the shape of the related Mössbauer spectra, but at the same time they increase the average amplitude of SDW.

B.4.2. The influence of strain

The \overline{H} values determined from the IIFD-curves based on Eq. (4.1) for strained \overline{H}_a and strain-free \overline{H}_b Cr-Sn alloys are displayed in Table III. Although the release of the strain has significantly changed the actual shape of the corresponding

TABLE II

TABLE III

Average hf field as determined from Eq. (4.1) for strained \overline{H}_a and strain-free \overline{H}_b samples of $\operatorname{Cr}_{100-y}\operatorname{Sn}_y$ alloys.

y	\overline{H}_a [kOe]	\overline{H}_{b} [kOe]
0.07	36.9	36.2
0.58	37.3	38.5
0.73	37.4	33.2
1.18	40.4	41.0

HFD-curves (see Ref. [14]), the values of \overline{H} remained practically unchanged. This is in contrast with the results found for the Cr-Mn alloys from which two samples were the subject of a release of strain, viz. the one with the lowest content of Mn and the other with the highest Mn concentration. In both cases the release of the strain resulted in the decrease in the \overline{H} -value, namely from $\overline{H}_a = 45.9$ kOe to 37.2 kOe for the former, and from $\overline{H}_a = 74.3$ kOe to 52.0 kOe for the latter. The lower values of \overline{H} for the strain-free samples are in quantitative agreement with the fact that strain increases the Néel temperature of the system.

B.4.1.3. Influence of a grain size

In the light of the results presented in Sec. A.4.3., we assume that the different shape of the Mössbauer spectra of Cr-Sn samples, shown in Figs. 5, 13, 14 and 15, is due to a different microstructure of the samples and particulary to a different size of grains.

A further independent support in favour of such supposition can be found in the shape of the spectra registered for Cr-Mn alloys (Fig. 11). All samples of Cr-Mn studied were polycrystalline, their grains had a similar size (10-60 μ m) and in all corresponding spectra, but one, viz. the one registered for the most concentrated sample, there is a characteristic central single-line subspectrum. What, however, distinguishes this particular sample from the other three in respect to the properties of SDW, is a commensurability of SDW. The most concentrated sample is almost in the commensurate state and the central single-line subspectrum does not exist in its spectrum, while the less concentrated three samples are still in the incommensurate state and the subspectrum does exist.

In the light of these observations the following conclusion can be drawn as far as the existence of the central single-line subspectrum in Mössbauer spectra of chromium and its alloys is concerned: this spectrum is an indication that the sample is polycrystalline and SDW are incommensurate. The spectra registered for polycrystalline Cr-Sn samples with a different size of grains give evidence that the relative contribution of this subspectrum depends on the size of grains. Namely, the smaller the grain size, the larger the contribution of the central subspectrum is. Obviously, grain boundaries interect with SDW modyfying thereby their shape. If now one assumes that the single-line subspectrum reflects these interactions, one comes to a conclusion that these interactions have a pinning character. SDW seems to have nodes on the grain boundaries which manifest itself in the Mössbauer spectrum just by a single line. Such a picture would be consistent with the present observations concerning the correlation between the size of grains and the relative contribution of the central single-line subspectrum.

Modified SDW, e.g. by additional nodes, can formally be described in terms of higher-order harmonics. In Sec. 2.4. of this paper it was shown that the 3rd-order harmonic manifests itself in the Mössbauer spectrum through additional single-line subspectrum, provided its sign is negative (see Fig. 5a). Another feature of the Mössbauer spectra related to this harmonic is an increase of the maximum hf field (see Fig. 3 and 4). If therefore the present interpretation of the experimental spectra for Cr-Sn alloys is correct, then an increase of the maximum field with the decrease in the size of grains should be observed. Figure 16, where IIFD-curves



Fig. 16. HFD-curves obtained from the Mössbauer spectra of Cr-Sn samples: (a) from the spectrum in Fig. 13, (b) from the spectrum in Fig. 15, (c) from the spectrum in Fig. 14 and (d) from the spectrum in Fig. 5 (the sample containing 0.73 at% Sn).

for the samples involved are presented, gives a clear evidence in favour of this interpretation. The IIFD-curve labelled with (a) stands for a single-crystal sample while the other three labelled with (b), (c) and (d) were derived from the spectra of polycrystalline samples in the sequence of a decreasing size of grains from 60-200 μ m for (b) to 10-60 m for (d).

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