

First Mössbauer-effect evidence of the spin-flip phenomenon in metallic chromium

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We report the first successful measurement of the so-called spin-flip transition in metallic chromium with the ^{119}Sn nuclei Mössbauer effect. It occurs at $T_{\text{SF}} = 123\text{ K}$ when heating the sample and at $T_{\text{SF}} \approx 110\text{ K}$ when cooling the sample.

The so-called spin-flip (SF) transition in metallic chromium has already been observed with neutron scattering,¹ torque,² susceptibility,³ thermal expansion and magnetostriction,^{4,5} Young's modulus,⁶ the time-differential perturbed-angular correlation techniques (TDPAC),⁷ and ultrasonic attenuation⁸ and elastic constants⁹ experiments. It appears at $T_{\text{SF}} \approx 123\text{ K}$ and is usually described as a transition between transversely (T) and longitudinally (L) polarized spin-density waves (SDW). Recent experiments indicate, however, that the problem is not so simple, since strain waves¹⁰ (SW) and probably charge-density waves¹¹ (CDW) coexist

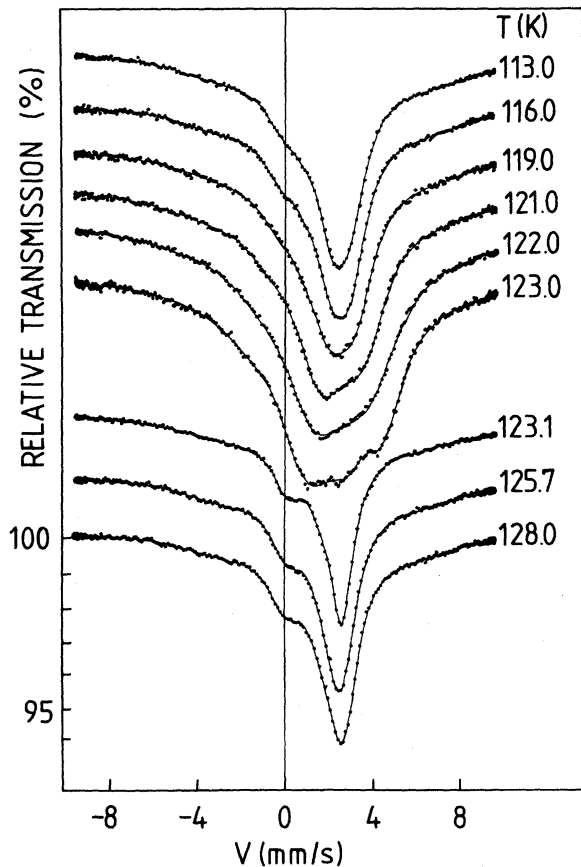


FIG. 1. ^{119}Sn nuclei Mössbauer spectra of Cr-0.4 at. % Sn for different increasing temperatures T .

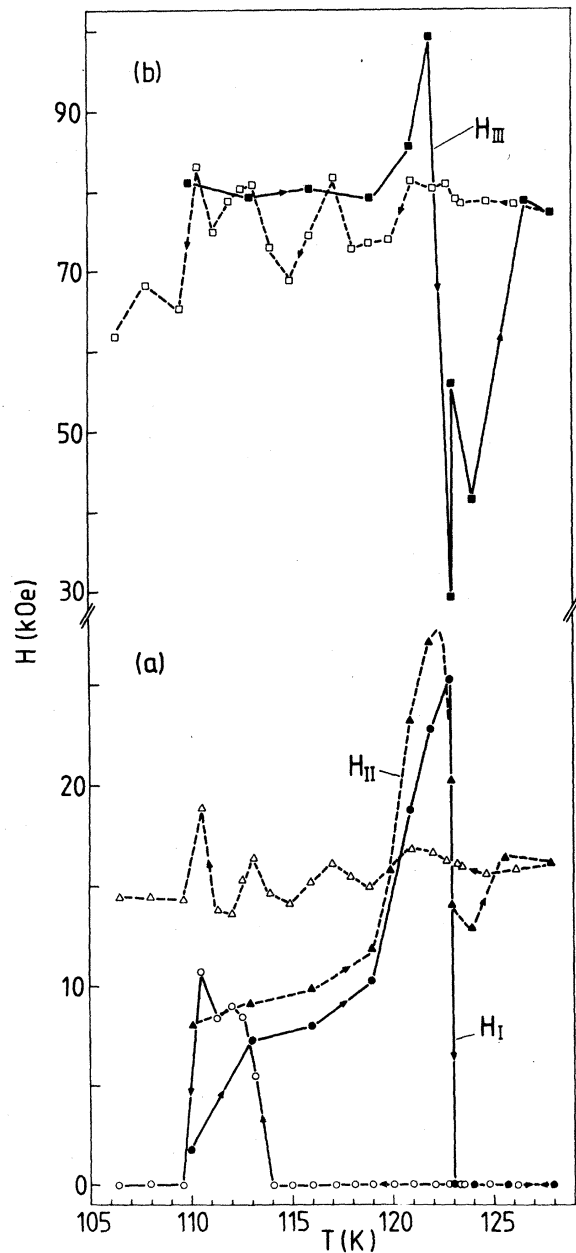


FIG. 2. Hyperfine fields (a) $H_{\text{I,II}}$ and (b) H_{III} vs increasing (full marks) and decreasing (open marks) temperature T .

in chromium with SDW. Moreover, TDPAC (Ref. 7) and the ultrasonic attenuation experiments⁸ showed that the transition itself is more complex than previously thought.

The Mössbauer effect (ME) is potentially a very suitable method for studying the SF transition as well as the coexistence of SDW and CDW. First attempts to observe the transition with ME were made by Wertheim,¹² who used the effect at ⁵⁷Fe nuclei dissolved in chromium and observed a single line in the whole temperature range studied (4–300 K). Street and Window,¹³ and Street, Munday, Window, and Williams,¹⁴ observed some structure in spectra using the effect at ¹¹⁹Sn nuclei. Nevertheless, they did not detect any change in the Mössbauer spectrum at T_{SF} .

In our experiment we have also used ¹¹⁹Sn nuclei in a sample of Cr–0.4 at.% Sn obtained by arc melting 99.999%

purity chromium with Sn enriched to $\sim 91\%$ in ¹¹⁹Sn isotope. However, contrary to the previous experiments we carried out an absorber experiment using CaSnO₃ as a source of 23.9-keV γ rays. For the ME measurements the bulk sample was filed to an average particle size of ~ 60 μm and was of $\sim 1\text{-mg}$ ¹¹⁹Sn per cm^2 thickness. The sample was placed in a cryostat and the temperature was controlled to an accuracy of better than ± 0.1 K. The Mössbauer spectra were registered by a conventional spectrometer having a 512-channel analyzer.

The sample was first cooled down to about 5 K and the measurements performed with increasing temperature. The run of each spectrum lasted for 24–36 h and Fig. 1 shows the spectra for the temperature range of interest. The effect of temperature on the spectra is obvious and it is clear that the SF transition occurs between 123 and 123.1 K. After reaching about 140 K the measurements were repeated with decreasing temperature. The spectra show a definite hys-

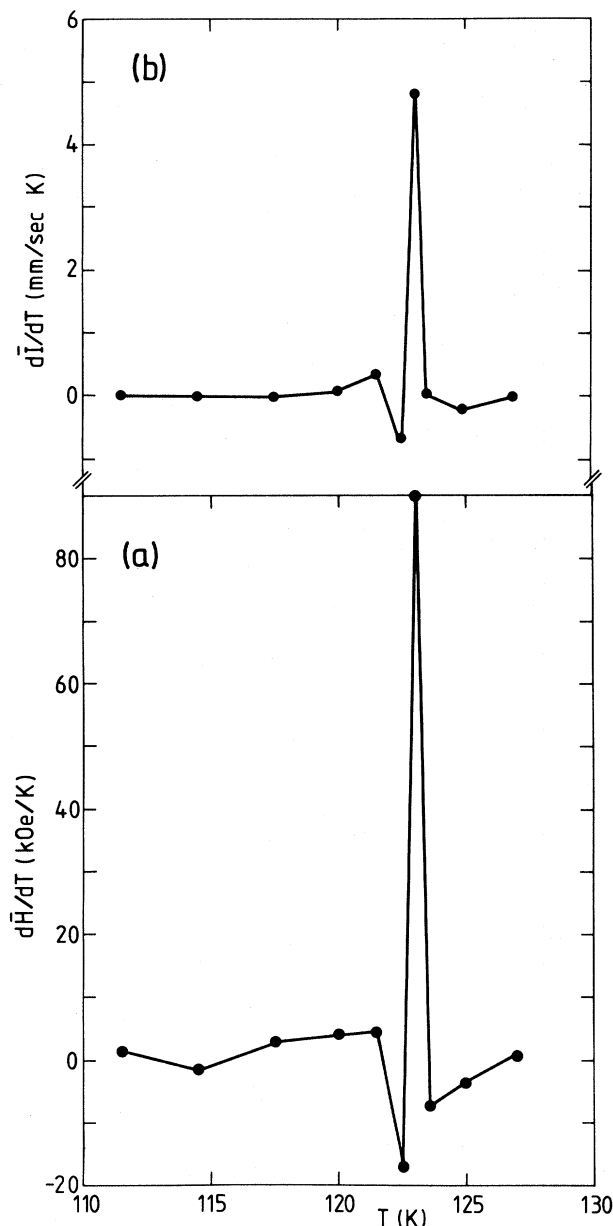


FIG. 3. Temperature derivative of (a) the average hf field $d\bar{H}/dT$ and of (b) the average isomer shift $d\bar{I}/dT$ vs temperature T .

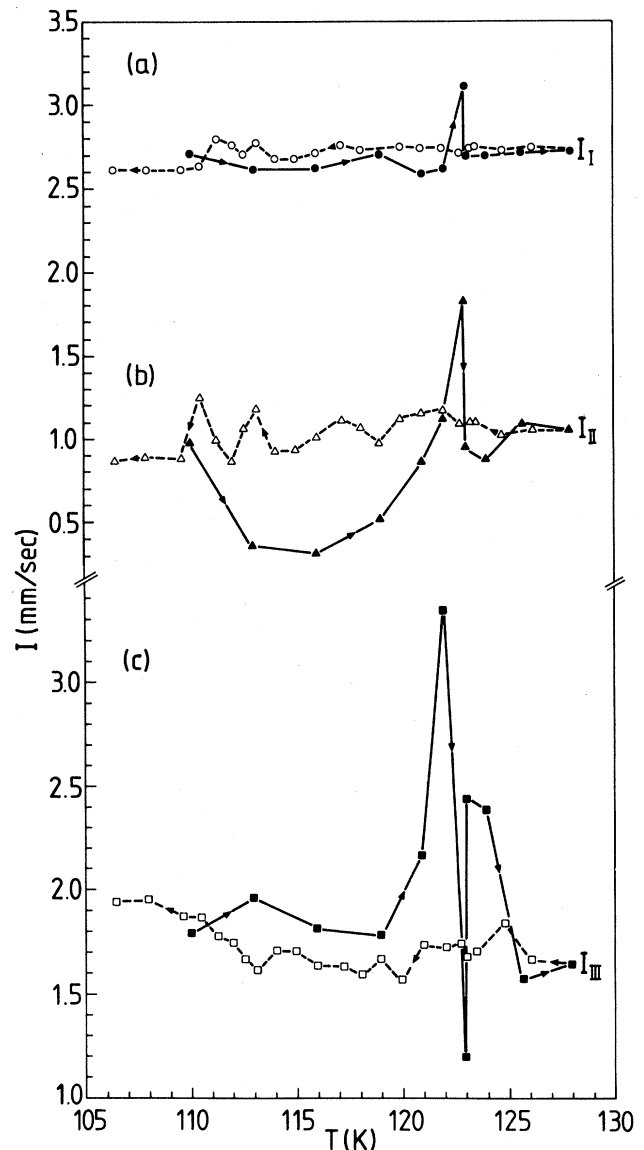


FIG. 4. Isomer shifts (a) I_I , (b) I_{II} , and (c) I_{III} vs increasing (full marks) and decreasing (open marks) temperature T .

teresis as the transition temperature is now shifted downwards by about 10 K.

To discuss the measured effects in a more quantitative way, all the spectra were computer fitted assuming that they consist of three subspectra, I and II having smaller splittings and corresponding to an atomic configuration with one Sn atom and with two Sn atoms in the vicinity of the probe nucleus and III with large splitting, which corresponds to ^{119}Sn nuclei having in their vicinity no Sn atoms. Each subspectrum was described by the corresponding hyperfine field H_i , isomer shift I_i , quadrupole splitting Q_i , probability P_i , and the linewidth Γ_i ($i = \text{I, II, III}$) having Lorentzian shape. The analysis showed that the P_i were temperature independent, indicating that the analysis in terms of the three subspectra is adequate. Their values are 0.26, 0.13, and 0.61, respectively, instead of 0.001, 0.031, and 0.969 as expected for a random distribution. Therefore, rather a high degree of clustering of Sn atoms occurs. In the following, we discuss the temperature dependence of the hyperfine (hf) field and isomer shift parameters.

Figures 2(a) and 2(b) show the hf fields $H_{\text{I,II,III}}$ versus increasing (full marks) and decreasing (open marks) temperature. One readily can see a sharp change of all three components at $T_{\text{SF}} \approx 123$ K. An effect is already noticeable in the sample at $T \geq 110$ K as the hf fields and especially $H_{\text{I,II}}$ terms begin to increase smoothly at $T \geq 110$ K. When decreasing the temperature the picture is quite different. Firstly, the hf fields do not follow their previous routes, i.e., the phenomenon is not reversible and, secondly, the SF transition is not as sharp and occurs between 110–114 K. In addition, H_{II} and H_{III} exhibit irregular oscillations. Increasing the temperature again showed that $H_{\text{I,II,III}}$ followed other paths. The behavior of the hf fields, being a measure of SDW, therefore seems to be completely irreversible, i.e., by each measurement the hf fields, and hence the corresponding spin densities, have different values. Drastic changes in the SDW which occur around 123 K can also be visualized by plotting the temperature derivative of the

average hf field, $d\bar{H}/dT$ versus temperature T [see Fig. 3(a)].

Figures 4(a)–4(c) give evidence that also the isomer shifts $I_{\text{I,II,III}}$, being a measure of the s -electron charge density, show a similar behavior to that of the hf fields. It means that if we associate CDW with the isomer shift, we must conclude (a) that also CDW undergoes the SF transition at $T_{\text{SF}} \approx 123$ K, (b) that CDW must be incommensurate as the measured isomer shifts also exhibit similar behavior to that of the hf fields. The temperature derivative of the average isomer shift $d\bar{I}/dT$ also shows a clear peak at $T_{\text{SF}} \approx 123$ K [Fig. 3(b)].

Finally, we note that there is a difference between the measured quantities for L SDW and T SDW. From Figs. 2 and 4 it follows, namely, that $\Delta H_{\text{I}} = H_{\text{I}}^T - H_{\text{I}}^L \approx -7$ kOe, $\Delta H_{\text{II}} = H_{\text{II}}^T - H_{\text{II}}^L \approx +7$ kOe, $\Delta H_{\text{III}} = H_{\text{III}}^T - H_{\text{III}}^L \approx -10$ kOe. The differences in the corresponding isomer shifts are $\Delta I_{\text{I}} \approx +0.1$ mm/sec, $\Delta I_{\text{II}} \approx +0.5$ mm/sec, $\Delta I_{\text{III}} \approx +0.6$ mm/sec. This means that for the all three cases the charge density increases after the SF transition takes place, while the spin density decreases for the components I and III and increases for the component II. As the hf field changes can be regarded as changes in the amplitude of SDW and changes in the isomer shift reflect changes in the amplitude of CDW, the above observation may indicate that the correlation between SDW and CDW is not as simple as that between SDW and SW.¹⁰ The different values of the hf fields (revealed also by the TDPAC measurements⁷) and isomer shifts before and after the SF transition may also indicate a change in the modulation of both SDW and CDW.

We hope that further ME study, in particular on single-crystal samples, will bring more insight into this problem.

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