

## Mössbauer study of the ferromagnetic behavior of chromium-rich Fe-Cr alloys\*

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Mössbauer spectra have been obtained as a function of temperature for  $\text{Fe}_x\text{Cr}_{1-x}$  alloys with  $x = 0.20, 0.25,$  and  $0.30$ . Analysis of the line widths yields Curie temperature values of 60, 160, and 260 K, respectively, in agreement with bulk magnetization measurements. The results show a broad distribution of hyperfine fields indicating a wide variation of iron magnetic moment values from site to site. This result is consistent with neutron-diffraction and Mössbauer experiments on alloys of higher Fe concentration. The most probable hyperfine field and the bulk magnetization follow a temperature dependence proportional to  $(1 - T/T_c)^{1/2}$ .

### INTRODUCTION

The magnetic properties of  $\text{Fe}_x\text{Cr}_{1-x}$  solid-solution alloys in the concentration range near  $x = 0.25$  have been the subject of a number of investigations. Bulk magnetization measurements in the range  $x > 0.30$  show that the alloys are normal ferromagnets,<sup>1-3</sup> and the concentration dependence of the transition temperatures indicates that  $T_c$  approaches zero as  $x$  decreases below 0.20. Recent neutron-diffraction measurements<sup>4</sup> suggest that in this concentration region the magnetization is inhomogeneous, with the magnetic moment largely concentrated on the Fe atoms but with a magnitude which varies greatly with atomic environment.

In principle, the Mössbauer effect of  $^{57}\text{Fe}$  can be utilized effectively to investigate an inhomogeneous magnetization distribution, inasmuch as the hyperfine field present at the Fe site is frequently strongly dependent on the neighboring environment. Indeed, such a study has been carried out in detail by Schwartz and Chandra<sup>5</sup> for Fe-Cr alloys with  $x \geq 0.40$ . In that study, a large distribution of hyperfine fields was seen, and the data were analyzed on the basis of a simple statistical model. Some Mössbauer measurements have been performed on alloys in the critical concentration region;<sup>6-8</sup> however, a comparison of the various results indicates differences in the samples used. Some of these differences may arise from the presence of short-range nonrandomness in the distribution of atoms. Such effects are clearly seen in the neutron-diffraction experiments.<sup>4</sup>

We present here Mössbauer measurements at  $^{57}\text{Fe}$  nuclei for  $\text{Fe}_x\text{Cr}_{1-x}$  alloys with  $x = 0.30, 0.25,$  and  $0.20$ . The sample preparation techniques were identical to those used for recent bulk magnetization,<sup>2</sup> neutron-diffraction,<sup>4</sup> and critical-point studies.<sup>9</sup>

### EXPERIMENTAL DETAILS

The alloys were arc melted in a helium-argon atmosphere with 99.99-wt. % pure starting materials. The resultant buttons (weighing  $\sim 5$  g) were given homogenization heat treatments for one week at 1150 °C, followed by one week at 825 °C, and then were water quenched. The buttons were cut and filed, and the resultant powder was given a strain-relief anneal at 825 °C for 8 h and water quenched.

Mössbauer spectra were obtained using a 25-mCi source of  $^{57}\text{Co}$  in a Cu matrix that was held at room temperature. Absorbers, with thicknesses equivalent to  $\sim 5$  mg/cm<sup>2</sup> of natural iron, were cooled in a cold-finger Dewar, and the temperature was measured by carbon and platinum resistance thermometers.

### RESULTS AND ANALYSIS

The temperature dependence of the Mössbauer spectra for the  $x = 0.25$  sample is shown in Fig. 1. The two predominant features are (1) the appearance of a magnetic transition, as evidenced by the hyperfine splitting  $H$  beginning at  $T \sim 160$  K, and (2) the severe line broadening in the fully developed hyperfine pattern at low temperature. The latter is characteristic of a distribution of hyperfine fields in the material. The data were analyzed by means of a procedure developed by Window.<sup>10</sup> In this method, it is assumed that the observed line shapes are reproduced by a continuous probability  $P(H)$  for the distribution of hyperfine fields. A computer program was devised that deconvolutes the spectra to obtain  $P(H)$  by means of a form of Fourier inversion. As originally written by Window and as used here, this procedure presumes that quadrupole interactions are negligible and a single isomer shift value exists for all hyperfine

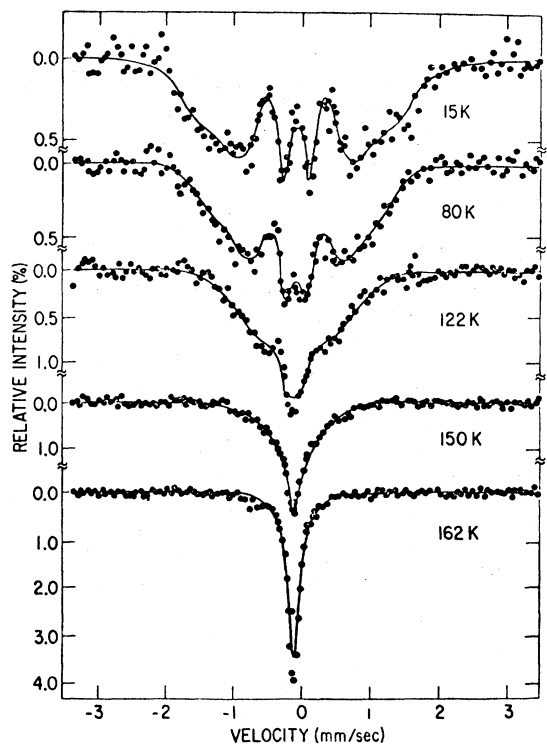


FIG. 1. Mössbauer spectra vs temperature for  $\text{Fe}_{0.25}\text{Cr}_{0.75}$ . The solid lines show the results of least-squares fits using the procedures of Ref. 10.

fields. In some cases, these are troublesome assumptions. However, in the present case, a detailed investigation of the data shows that the quadrupole interactions are quite small, and, as a first approximation, we expect the severe line broadenings present to mask any distribution in isomer shifts (see discussion below). The Window method is advantageous because it makes no assumption about the origin of the hyperfine field distribution. Moreover, once  $P(H)$  has been obtained, it can be easily compared with the predictions for relevant models. For cases in which individual hyperfine fields corresponding to different environments can be resolved, analysis by fitting a number of discrete spectra to the data is preferable. However, for data such as those discussed here, where random variations in local composition cause distributions of hyperfine fields with individual fields that cannot be resolved, the Window approach is more useful.

Fits to the Mössbauer data obtained by the Window approach are shown by the solid lines in Fig. 1. The resultant probability distributions are shown at various temperatures by the dotted lines in Fig. 2. As is common in numerical Fourier inversion procedures with a finite number of terms, oscillations occur in the tails of the dis-

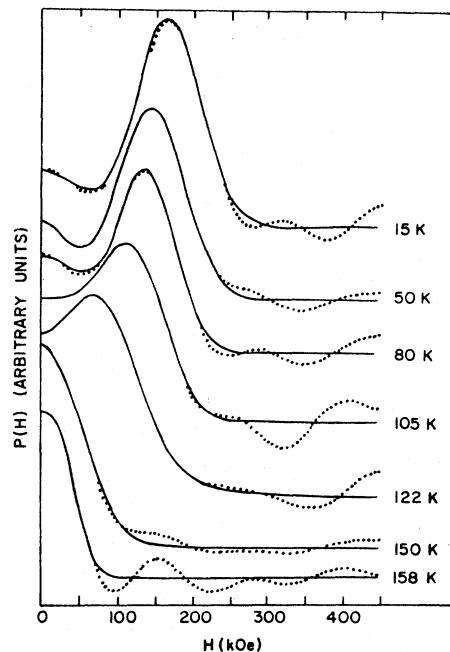


FIG. 2. Hyperfine field probability distribution curves  $P(H)$  obtained from the solid lines of Fig. 1 for  $\text{Fe}_{0.25}\text{Cr}_{0.75}$ .

tribution, which should not be considered physically meaningful. Ignoring these oscillations, the observed  $P(H)$  are characterized by a strong maximum at some value  $H_1$  that is temperature dependent and approaches zero as the magnetic transition temperature is approached. In addition, a weaker maximum occurs near  $H=0$  even at the lowest temperatures. To quantify these results, we have assumed that  $P(H)$  is composed of two Gaussians, one centered at  $H=0$  and the other at  $H_1$ . The widths of the Gaussians, their amplitudes, and the value of  $H_1$  were then varied in a least-squares fitting routine to obtain the solid lines shown in Fig. 2. First, however, it is useful to discuss the origin of  $P(H)$  and to compare the results of the present procedure with the discrete approach to the analysis of such data.

Schwartz and Chandra<sup>5</sup> investigated hyperfine field distributions for a number of  $\text{Fe}_x\text{Cr}_{1-x}$  alloys with compositions ranging from  $x=0.40$  to  $0.76$ , i.e., somewhat more concentrated than the present alloys. Their results were interpreted according to a model that has frequently been used for random magnetic alloys. It is assumed that the hyperfine-field distribution is due to the variation in near-neighbor environments, with any one Fe atom showing a hyperfine field

$$H(x, n, m) = H_{\text{Fe}} (1 + an + bm)(1 + kx). \quad (1)$$

Here,  $H_{\text{Fe}}$  is the hyperfine field in Fe metal,  $n$  is

the number of nearest Cr neighbors,  $m$  is the number of next-nearest Cr neighbors,  $a$  and  $b$  are constants, and  $k$  is a constant that takes into account overlap effects between neighboring solute atoms. The spectrum for a given alloy is then analyzed by calculating a number of spectra for different near-neighbor environments, weighting them according to random distribution requirements, and using a fitting procedure to determine values of  $a$ ,  $b$ , and  $k$ . At temperatures well below the transition temperature, Schwartz and Chandra found the data were described by  $a=b=-0.56$  for  $x=0.76$ ,  $a=b=-0.52$  for  $x=0.40$ , and  $kx=0.05$  for both.

Figure 3 shows  $P(H)$  for the  $x=0.25$  alloy at 15 K obtained in the present work. In addition, we show by the bar diagram the probability distribution obtained from Eq. (1) and the assumption of random distribution, with  $a=b=-0.48$  and  $kx=0.05$ . It is clear from this comparison that the major peak in  $P(H)$  can be easily explained as being due to the variations in near-neighbor environment. The present analysis provides information compatible with that obtained by the method of fitting many discrete spectra to the data, and as Fig. 3 shows, the values obtained to characterize the field distributions are consistent with those obtained for lower Fe concentrations by the other method. It is also clear, however, that such an approach cannot explain the smaller peak near  $H=0$ . We note that Schwartz and Chandra also ignored quadrupole interactions in their analysis, but found it necessary to include some variation of isomer shift with the number of Fe atoms in near-neighbor and next-near-neighbor sites to obtain good fits to their data. Such a variation has not been included in the present analysis. If present, it will

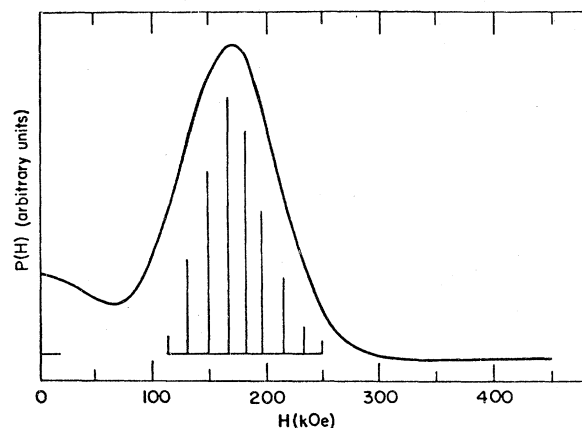


FIG. 3. Comparison of the probability distribution  $P(H)$  with the discrete calculation (bar diagram) based on Eq. (1) for  $\text{Fe}_{0.25}\text{Cr}_{0.75}$ .

be most noticeable as a broadening of the relatively sharp inner lines rather than of the already severely broadened outer lines, and, in the Window procedure, this might be interpreted as a variation in small hyperfine field values. However, estimates based on Schwartz and Chandra's value for the change in isomer shift due to Cr neighbors ( $-0.022$  mm/sec for each nearest or next-nearest neighbor) show that this effect cannot produce as broad a distribution in hyperfine field as observed around  $H=0$  (Fig. 3).

#### DISCUSSION

The essential information about the magnetically ordered iron atoms obtained from the present work is summarized by the values of  $H_1$  and  $\Delta H$  the position of the major peak in the  $P(H)$  distribution and its width, respectively. Magnetic transition temperatures for the three alloys have been determined by plotting the width  $\Delta H$  as a function of temperature above and just below  $T_c$ . In all cases, an increase in  $\Delta H$  occurs as one enters the magnetic state, and the increase yields the values of  $T_c$  listed in Table I. Within experimental error, the transition temperatures are in agreement with the values obtained from magnetization measurements on these samples.<sup>9</sup> Saturation values for the most probable hyperfine field  $H_1$  are also given in Table I. Neutron-diffraction measurements<sup>4</sup> show that the distribution of the magnetic moment is primarily on the Fe atoms, with essentially no Cr moment in the concentration range encompassed by the present study. Values of the mean moment, obtained from magnetization measurements,<sup>9</sup> are also listed in Table I and are seen to vary monotonically (although not linearly) with the hyperfine field.

The temperature dependence of  $H_1$  and the bulk magnetization are given in Fig. 4 for the three samples. Below  $T_c$ ,  $\Delta H$  is essentially independent of temperature and concentration, with a value of  $\sim 40$  kOe for each alloy. The variations in near-neighbor environment throughout the material give rise to a distribution of hyperfine fields. At low temperatures, this distribution produces a spread

TABLE I. Measured transition temperatures  $T_c$  and saturation values for the most probable hyperfine field  $H_1$  for  $\text{Fe}_x\text{Cr}_{1-x}$  alloys. Also given are bulk magnetic moment values  $\bar{\mu}_0$  from Ref. 9.

$x$	$T_c$ (°K)	$H_1$ (kOe)	$\bar{\mu}_0$ ( $\mu_B$ /atom)
0.20	$60 \pm 5$	$112 \pm 10$	0.17
0.25	$160 \pm 5$	$180 \pm 5$	0.40
0.30	$260 \pm 10$	$190 \pm 5$	0.55

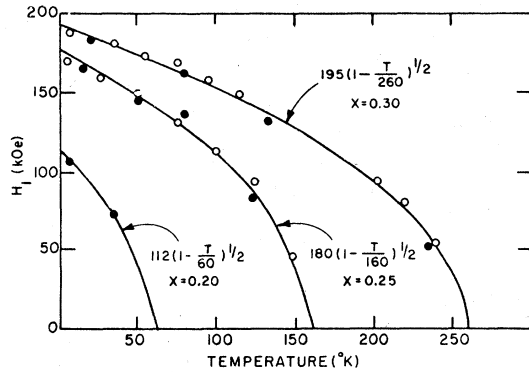


FIG. 4. Temperature dependence of the most probable hyperfine field  $H_1$  (solid circles) for the indicated  $\text{Fe}_x\text{Cr}_{1-x}$  alloys. Open circles are bulk magnetization values, which have been normalized to give the same saturation value as the corresponding hyperfine field.

in the saturation values of the hyperfine field. If the material has a common ordering temperature for all ions (appropriate for an alloy in this concentration range) and if the temperature dependence of the hyperfine field for all ions is identical, then  $H_1$  should follow this temperature dependence and  $\Delta H$  should steadily *decrease* as one goes from low temperatures to  $T_c$ . However, the variations in near-neighbor environment also cause a distribution in exchange fields throughout the materials, and, as a result, different ions may have hyperfine fields that show quite different temperature dependences.<sup>11-13</sup> In general, this will have a tendency to cause  $\Delta H$  to *increase* as the temperature increases, and  $H_1$  will then follow some average temperature dependence. Which of the above mechanisms is dominant in any given case is difficult to decide *a priori*. In the present study, the width is found to be approximately the same for all concentrations and temperatures. The temperature dependence of  $H_1$  can be characterized *empirically* by

$$H_1 = H_1^{\text{sat}}(1 - T/T_c)^{1/2} \quad (2)$$

as shown in Fig. 4.

The broad distribution of hyperfine field values found in the present study is consistent with previous neutron diffraction,<sup>4</sup> magnetization,<sup>9</sup> and Mössbauer<sup>5</sup> results, which indicate an inhomogeneous distribution of magnetic moment, i.e., the magnitude of the moment at any particular iron site is strongly dependent on its local environment. Although the minor peak in the  $P(H)$  distribution at  $H=0$  may be an artifact, as noted earlier, it is likely that in this concentration range, iron atoms with no magnetic moment are present. From the areas under the two peaks (Fig. 3), we would estimate this concentration to be ~15% of the iron atoms, which is close to the probability (in this composition range) that an iron atom has all eight nearest-neighbor chromium atoms. Nevertheless, each of the alloys appears to undergo a bulk transition to ferromagnetism at a reasonably well-defined temperature.

#### CONCLUSIONS

Mössbauer experiments have been performed on  $\text{Fe}_x\text{Cr}_{1-x}$  alloys with  $x=0.20, 0.25,$  and  $0.30$ . Magnetic ordering is observed with transition temperatures that are in agreement with those obtained from bulk magnetization measurements. The data have been analyzed to yield the distributions of hyperfine fields  $P(H)$  in the materials, and the results can be summarized as follows:  $P(H)$  can be described primarily by one major Gaussian peak with a width arising from the variation of near-neighbor environments in the samples. This width  $\Delta H$  is found to be constant in temperature for all samples, and the peak position  $H_1$  follows the simple temperature dependence of Eq. (2).

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