

tion, ESR studies<sup>33</sup> on the relaxation time for the  $\Delta M=1$  transition of  $\text{Fe}^{+2}$  in  $\text{MgO}$  also indicate an Orbach process with  $\Delta=92.5 \text{ cm}^{-1}$ . The discrepancy in the value for  $\Delta$  measured by optical methods as compared with ESR (and Mössbauer) evaluation may be explained by the effect of finite width of the excited level.<sup>34</sup>

Our derived relaxation frequencies (Fig. 5) deviate from the exponential dependence on  $1/T$  at  $\sim 12^\circ\text{K}$ . The spin-lattice relaxation time for  $\text{Fe}^{+2}$  in  $\text{MgO}$  determined by ESR experiments<sup>33</sup> was found to be described by a one-phonon direct process at the lowest temperatures, but the direct process is not dominant until  $T < 8^\circ\text{K}$  (the solid curve in Fig. 5). The origin of the difference is not explained, but it may be as-

<sup>33</sup> R. L. Hartman, E. L. Wilkinson, and J. G. Castle, Jr., *Bull. Am. Phys. Soc.* **12**, 642 (1967).

<sup>34</sup> B. A. Young and H. J. Stapleton, *Phys. Letters* **21**, 498 (1966).

sociated with the concentration of iron in the  $\text{MgO}$ , or some other sample-dependent effect.

#### ACKNOWLEDGMENTS

It is a pleasure to acknowledge the valuable aid of M. Blume in providing us with the mathematical apparatus required to describe the relaxation process and for his efforts in explaining the details to us, as well as for several illuminating discussions on other aspects of this problem. We are particularly grateful to F. S. Ham for acquainting us with his work prior to publication and for a number of subsequent discussions about these experiments and their interpretation. His continued interest is appreciated. Thanks are also due to R. B. Frankel and J. Y. Wong for informing us of their results before publication, to D. W. Freeman, who programmed the data-fitting codes and kept them running, and to R. Booth for continuing help with the experimental operation.

## Hyperfine Fields and Electronic Structure of CsCl-Type Ternary Alloys of the First Transition Series

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The  $^{59}\text{Co}$  Knight shift  $K$  and the  $^{57}\text{Fe}$  isomer shift have been measured in  $\text{TiFe}_{1-x}\text{Co}_x$  alloys over most of the composition range  $0 \leq x \leq 1$ . The experimental results are discussed in terms of correlations with electron concentration and  $s$  admixture in the  $d$  bands. At room temperature,  $K$  varies from a maximum of  $(3.2 \pm 0.2)\%$  at  $x \approx 0.8$ , and roughly follows the electronic specific heat as the composition is varied, with a minimum of  $K = (0.8 \pm 0.2)\%$  near  $x = 0$ .  $K$  increases substantially as the temperature is lowered for  $x$  near 1, and decreases somewhat for  $x$  near 0. The maximum  $K$  measured is  $(4.7 \pm 0.2)\%$  for  $x \approx 0.8$  at  $120^\circ\text{K}$ . The slopes of  $K$  versus susceptibility vary from  $+86 \text{ kG}/\mu_B$  per formula unit for  $x = 0.8$  to  $-47 \text{ kG}/\mu_B$  per formula unit for  $x = 0.05$ . The isomer-shift variation, from  $-0.15 \pm 0.01$  (mm/sec relative to pure Fe) at  $\text{TiFe}$  to  $-0.19 \pm 0.02$  at  $\text{TiCo}$ , is similar to that of Fe in Cr-Mn. The  $^{47,49}\text{Ti}$  Knight shift in  $\text{TiFe}$  is  $(0.26 \pm 0.04)\%$  at room and at liquid-nitrogen temperatures.

### I. INTRODUCTION

THE CsCl-type pseudobinary alloy system  $(\text{TiFe})_{1-x}(\text{TiCo})_x$  formed from the two transition-metal intermetallic compounds  $\text{TiFe}$  and  $\text{TiCo}$  exhibits a variety of surprising features. Although neither  $\text{TiFe}$  nor  $\text{TiCo}$  is ferromagnetic above  $1^\circ\text{K}$ , ferromagnetism with paramagnetic Curie points of about  $50^\circ\text{K}$  is observed<sup>1</sup> in the composition range  $0.3 \leq x \leq 0.7$  with the exception of  $x = 0.5$ . The alloy  $\text{TiFe}_{0.5}\text{Co}_{0.5}$  does not order magnetically above  $1.2^\circ\text{K}$  but exhibits a superconductive transition<sup>1</sup> at about  $3^\circ\text{K}$ . The electronic specific

heat values  $\gamma$  for these alloys<sup>2</sup> display a remarkable parallelism, as shown in Fig. 1, with the values of  $\gamma$  appropriate to the first transition series bcc alloys having the same average conduction (or "valence") electron concentration per atom  $n_e$ . The terms electron concentration and electron-to-atom ratio (often abbreviated  $e/a$ ), are used interchangeably.

The Mössbauer effect for  $^{57}\text{Fe}$  in  $\text{TiFe}_{1-x}\text{Co}_x$  shows<sup>3</sup>

<sup>2</sup> E. A. Starke, Jr., C. H. Cheng, and P. A. Beck, *Phys. Rev.* **126**, 1746 (1962); C. H. Cheng, C. T. Wei, and P. A. Beck, *ibid.* **120**, 426 (1960); C. H. Cheng, K. P. Gupta, E. C. Van Reuth, and P. A. Beck, *ibid.* **126**, 2030 (1962).

<sup>3</sup> L. H. Bennett and L. J. Swartzendruber, *Phys. Letters* **24A**, 359 (1967); L. J. Swartzendruber and L. H. Bennett, *Bull. Am. Phys. Soc.* **12**, 349 (1967). Note that the designation of the alloys and the isomer shift reference and sign convention are different in this paper.

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† Supported by U.S. Atomic Energy Commission.

<sup>1</sup> B. F. DeSavage and J. F. Goff, *J. Appl. Phys.* **38**, 1337 (1967).

no resolvable magnetic hyperfine structure and no discernible difference in linewidth between the ferromagnetic and nonferromagnetic regions. Contrasting with the magnetization<sup>1</sup> of 0.2 Bohr magnetons per formula unit, the Mössbauer line shape and width for a ferromagnetic sample below its Curie point indicate no homogeneous hyperfine field greater than 10 kG, a result which is surprising in both its smallness and its constancy with composition.

The present paper extends earlier <sup>57</sup>Fe isomer-shift studies and reports Co and Ti nuclear magnetic resonance (NMR) results for the alloys above their Curie temperature. The <sup>59</sup>Co NMR results show significant variation with alloy composition. The temperature dependence of the Knight shift  $K$  versus susceptibility  $\chi$  slopes varies within +86 to -47 kG per induced Bohr magneton per formula unit. The positive slope result is the largest seen to date for any metal or alloy system, and all the slopes, including the negative ones, display the not surprising result of significant  $s$  admixture in the  $d$  bands. One purpose of this paper will be to investigate the extent of this admixture.

The parallelism cited above between this system and the bcc sequence extends beyond specific heat behavior. For example, TiFe with an average of six electrons per atom outside of the argon core appears to be similar in many respects to the group VI element chromium. The electrical resistivity, thermoelectric power, and thermal conductivity of the  $(\text{TiFe})_{1-x-y}(\text{TiCo})_x(\text{TiNi})_y$  alloys have been discussed<sup>4</sup> in terms of a band structure primarily dependent on  $n_e$  varying from 6.0 (TiFe or Cr) to 7.0 (TiNi or Mn). The Hall effect in these

alloys has been discussed<sup>5</sup> in terms of the band structure of the corresponding elemental metals Cr, Mo, and W. Unusual mechanical properties<sup>6</sup> have been shown to be related to a unique martensitic transition viewed as a function of  $n_e$  from 6.0-7.0. The results to be reported in this paper display additional correlations with  $n_e$  and, in turn, the Cr-Mn system. These correlations, as well as the  $s$  admixture, will be of primary concern to us in this paper.

The  $\text{TiFe}_{1-x}\text{Co}_x$  alloy system displays other properties which, while of less immediate concern, deserve mention here. Considering<sup>7</sup> the systematics of the formation of CsCl structures in the transition elements, a correlation has been made between the lattice contraction in the intermetallic compound and the tendency to form a CsCl structure. The lattice contraction is taken as a measure of the "bond strength" between unlike atoms, leading to the conclusion that the bond strength increases through the series TiNi, TiCo, and TiFe. Accompanying this increase in bond strength is a reduction in the number of unpaired  $d$  spins on the Fe, Co, or Ni.

## II. EXPERIMENTAL

Samples were prepared by arc melting and crushing to powder. Details of the lineshapes, which are dependent on various aspects of sample preparation are discussed elsewhere.<sup>8</sup> Suffice it to say that neither the line position nor the linewidth is substantially affected by slight deviations from stoichiometry, by surface or internal oxidation, or strain disorder.

Mössbauer effect isomer shifts for  $\text{TiFe}_{1-x}\text{Co}_x$  were previously reported<sup>9</sup> to be approximately independent of composition. Extended measurements improving precision and plotted in Fig. 2 show a change in isomer shifts just outside experimental error from  $-0.15 \pm 0.01$  mm/sec at TiFe to  $-0.19 \pm 0.02$  mm/sec at TiCo relative to pure iron. It is interesting that both the magnitude and the change with  $n_e$  agree well with the isomer shift results given by Quaim<sup>9</sup> for a line drawn between Cr and Mn. If a change in  $n_e$  from 6 to 6.5 were to add one-half a  $d$  electron to an Fe site, there would be an isomer-shift change of about six times the observed change of  $-0.04$  mm/sec and of the opposite sign. It is, of course, not expected that increasing the  $n_e$  by 0.5 actually adds one-half a  $d$  electron to the Fe site and this fact, plus significant  $s$  admixture in the band involved, are responsible for the trend seen.

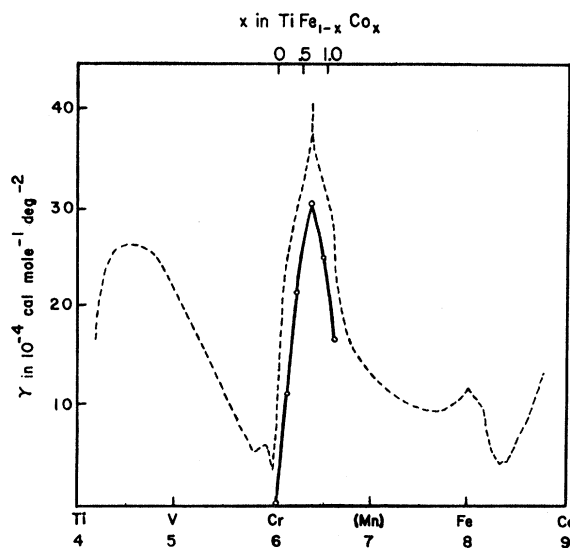


FIG. 1. Electronic specific heat  $\gamma$  versus average-valence electron concentration ( $n_e$ ). Dashed line is for bcc Ti-V, V-Cr, Cr-Fe, and Fe-Co alloys. Solid line is for TiFe-TiCo and TiCo-TiNi alloys.

<sup>4</sup> J. F. Goff, Symposium on TiNi and Associated Compounds, Naval Ordnance Laboratory, 1967 (unpublished); J. F. Goff, *Bull. Am. Phys. Soc.* **10**, 451 (1965).

<sup>5</sup> R. S. Allgaier, Symposium on TiNi and Associated Compounds, Naval Ordnance Laboratory, 1967 (unpublished).

<sup>6</sup> F. E. Wang and D. W. Ernst, Symposium on TiNi and Associated Compounds, Naval Ordnance Laboratory, 1967 (unpublished); F. E. Wang, *J. Appl. Phys.* **36**, 3232 (1965).

<sup>7</sup> M. V. Nevitt, in *Electronic Structure of Transition Metals*, edited by P. A. Beck (Interscience Publishers Inc., New York, 1963), p. 101.

<sup>8</sup> L. J. Swartzendruber and L. H. Bennett, Symposium on TiNi and Associated Compounds, Naval Ordnance Laboratory, 1967 (unpublished).

<sup>9</sup> S. M. Quaim, *Proc. Phys. Soc. (London)* **90**, 1065 (1967).

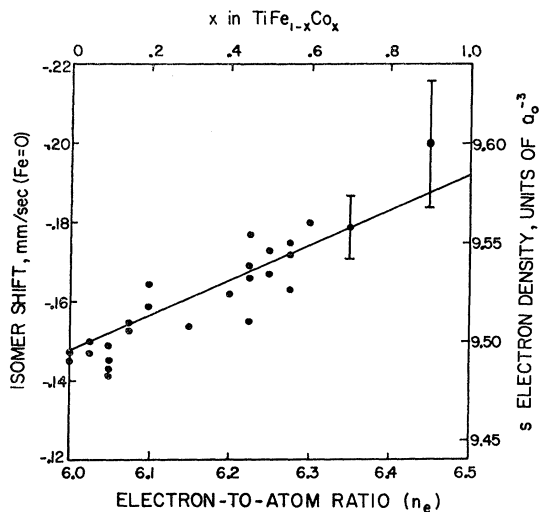


FIG. 2. The isomer shift as a function of  $x$  or  $n_e$  in  $\text{TiFe}_{1-x}\text{Co}_x$ . Isomer shifts are given relative to pure iron. The sign convention and electron density at the nucleus are from L. R. Walker, G. K. Wertheim, and V. Jaccarino, [Phys. Rev. Letters **6**, 98 (1961)]. The line is a least-squares fit to the observed points. The error bar for  $n_e=6.25$  is typical of all other points except for  $n_e=6.45$ , which has a larger error due to the low iron content.

Room-temperature  $^{59}\text{Co}$  Knight shifts<sup>10</sup> versus  $n_e$  ratios are plotted in Fig. 3. The magnitude of  $K$  shows large changes with composition and has a peak near  $n_e=6.4$  in the same region as the peaking of the electronic specific heat as shown in Fig. 1. In the region of nearly equal Fe and Co concentrations, the lines are very broad, have structure, and are somewhat asymmetric leading to large errors in choosing the center frequency (see Fig. 4). The structure suggests<sup>8</sup> satellite lines arising from varying local next-nearest-neighbor Fe-Co environments.

The Co Knight shift increases substantially as the temperature is lowered for  $x$  near 1 and decreases somewhat for  $x$  near 0.  $K$  versus  $\chi$  is plotted in Fig. 5 for five of the alloy compositions, with temperature as the implicit parameter, following the procedure of Clogston *et al.*<sup>11</sup> The slopes vary from  $+86 \text{ kG}/\mu_B$  per formula unit for  $x=0.8$  to  $-47 \text{ kG}/\mu_B$  per formula unit for  $x=0.05$ . None agree well with the field at a Co nucleus of approximately  $-140 \text{ kG}/\mu_B$  normally associated with  $3d$  core polarization alone. While this may be due, in part, to the distribution of the magnetization over the three types (Co, Fe, and Ti) of atomic sites, we believe it to be primarily associated with significant  $s$  admixture in the  $d$  bands over the full range of compositions, as will be discussed in the next section. Results for alloys of intermediate composition would be desirable but results of useful accuracy have not yet been obtained because, in addition to the

<sup>10</sup> A preliminary account has been presented by L. H. Bennett, L. J. Swartzendruber, and R. E. Watson, Bull. Am. Phys. Soc. **12**, 503 (1967).

<sup>11</sup> A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962); A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 779 (1961); A. Clogston, V. Jaccarino, and Y. Yafet, *ibid.* **134**, A650 (1964).

initial structure and asymmetry of the lines, large broadening occurred as the temperature was lowered. While broadening is possibly due to magnetic properties of disordered material, it is interesting to note a similar broadening<sup>12</sup> in the "itinerant" ferromagnetic material  $\text{ZrZn}_2$ .

The  $^{47,49}\text{Ti}$  NMR in TiFe has been measured.<sup>13</sup> The two isotopes  $^{47}\text{Ti}$  and  $^{49}\text{Ti}$  cannot be separated. The linewidth at 12 000 G is 30 G, whereas the separation between the two isotopes should be three G. The Knight shift is  $(+0.26 \pm 0.04)\%$  and is the same at room temperature and at liquid-nitrogen temperature. This value is, in turn, the same as the Ti Knight shift in  $\text{TiH}_2$ .<sup>14</sup> It has been seen in a number of cases,<sup>15</sup> that adding H to transition elements acts to increase the effective electron-to-atom ratio by one electron for each added H atom. Thus the  $n_e$  for  $\text{TiH}_2$  is 6, the same as for TiFe. The Knight shift for Ti in TiCo has been reported<sup>16</sup> to be much smaller,  $K=+0.08\%$ . The Ti Knight shift has not yet been measured in the intermediate alloys.

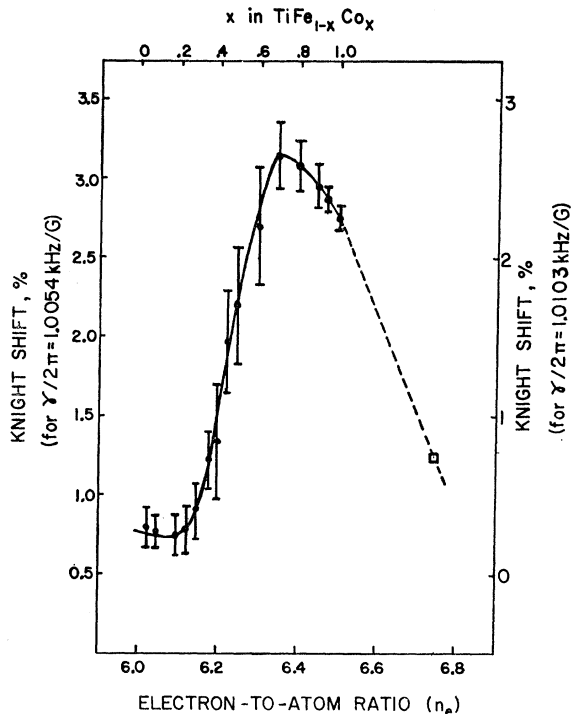


FIG. 3. Room-temperature  $^{59}\text{Co}$  Knight shifts in  $\text{TiFe}_{1-x}\text{Co}_x$  versus  $x$  or  $n_e$ . The value of  $K$  for TiCo agrees with G. W. West [Phil. Mag. **9**, 979 (1964)]. The open square is for  $\text{TiCo}_{0.5}\text{Ni}_{0.5}$  from West (Ref. 21). We use the value of  $K$  for  $\gamma/2\pi=1.0054 \text{ kHz/G}$  in the remainder of this paper.

<sup>12</sup> T. Yamadaya and M. Asanuma, Phys. Rev. Letters **15**, 695 (1965).

<sup>13</sup> A preliminary report was given by L. H. Bennett, Bull. Am. Phys. Soc. **11**, 330 (1966).

<sup>14</sup> R. A. Forman, Bull. Am. Phys. Soc. **10**, 606 (1965).

<sup>15</sup> See, for example, N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, England, 1936); H. Betsuyaku, Y. Takagi, and Y. Betsuyaku, J. Phys. Soc. Japan **19**, 1089 (1964); R. L. Zanowick and W. E. Wallace, J. Chem. Phys. **36**, 2060 (1962).

<sup>16</sup> L. E. Drain and G. W. West, Phil. Mag. **12**, 1061 (1965).

## III. DISCUSSION

A major feature of the  $^{59}\text{Co}$  Knight shifts is the occurrence of positive  $dK/d\chi$  slopes of significant magnitude for the Co rich alloys. While negative, the slopes of the Fe rich systems are significantly smaller than the approximately  $-140 \text{ kG}/\mu_B$  that would be expected if  $d$  "core polarization" were the only term contributing. As has already been indicated, we believe this behavior is associated with  $s$  admixture into the  $d$  bands. The occurrence of such admixing was recognized in the early band-theory considerations of the transition metals in the 1930's. In dealing with an almost unfilled, or better yet, almost filled  $d$  band metal (e.g., Pt and Pd), there is considerable justification in thinking of the band states, in the vicinity of the Fermi energy, as being either " $s$ - $p$ " or " $d$ " in character. When the Fermi energy falls in the middle of the  $d$  bands, as it does for the  $n_e$  ratios considered here, such " $s$ " character as there is largely appears admixed into states which are predominately  $d$ -like. There are hints<sup>17</sup> that this  $s$  admixture is important to the magnetic properties of transition metals.

The suggestion of the importance of  $s$  admixture is

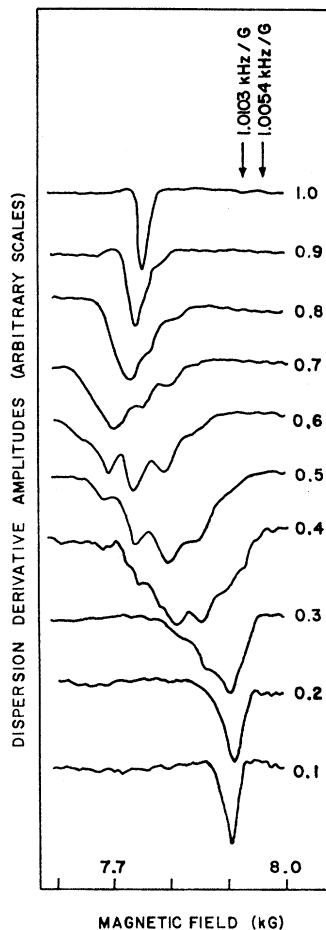


FIG. 4. Room-temperature NMR dispersion derivatives at 8,000 MHz for a number of alloys in the system  $\text{TiFe}_{1-x}\text{Co}_x$ . The value of  $x$  is shown next to each curve. The vertical scale varies with  $x$ .

<sup>17</sup> C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IV.

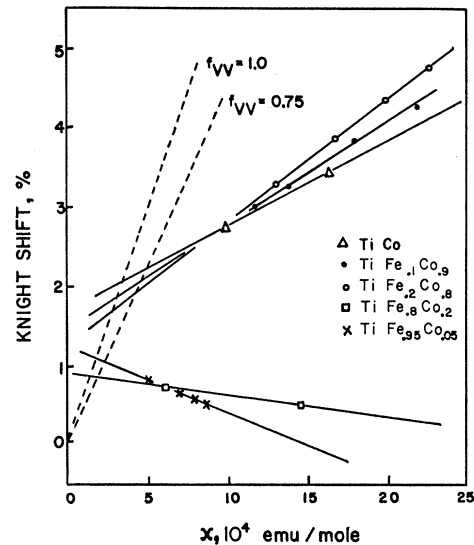


FIG. 5.  $^{59}\text{Co}$  Knight shift  $K$  versus susceptibility  $\chi$  diagram for five alloys of  $\text{TiFe}_{1-x}\text{Co}_x$ . The value of  $K$  for  $\gamma/2\pi = 1.0054 \text{ kHz/G}$  is used. The dotted lines are for two different values of the Van Vleck term.

not new to considerations of Knight shifts or to hyperfine fields in ferromagnetic metals. For example, it has been invoked by Saji *et al.*<sup>18</sup> in their study of the Knight shift in  $\text{TiBe}_2$ , by Yamadaya and Asanuma<sup>12</sup> for the  $^{91}\text{Zr}$  Knight shift in  $\text{ZrZn}_2$ , and by Brog *et al.*<sup>19</sup> in  $\text{MoCo}$  and  $\text{WCo}$  alloys. In each case, small negative  $dK/d\chi$  slopes<sup>20</sup> were obtained.

The above discussion has assumed that the temperature dependence of the susceptibility is associated with the  $d$ -band Pauli spin susceptibility, i.e., that

$$\chi = \chi_{\text{Pauli}}(T) + \chi_{\text{VV}} + \chi_{\text{dia}}, \quad (1)$$

where  $\chi_{\text{VV}}$  and  $\chi_{\text{dia}}$  are the orbital (or Van Vleck) and diamagnetic susceptibility, respectively, and are essentially independent of temperature. We have purposely omitted including a temperature-independent  $s$ -band Pauli term, such as normally appears in such expressions. In any case, the influence of this term on the Knight shift is small enough to be neglected. The temperature-dependent Knight shift is then attributed to the hyperfine field associated with the induced spin of the Pauli term. There is another possible source of temperature dependence which West<sup>21</sup> proposed when reporting his  $\text{CoTi}$  results, namely, a temperature-dependent orbital term.<sup>22</sup> This proposal becomes less

<sup>18</sup> H. Saji, T. Yamadaya, and M. Asanuma, *J. Phys. Soc. Japan* **21**, 255 (1966).

<sup>19</sup> K. C. Brog, W. H. Jones, Jr., and J. G. Booth, *J. Appl. Phys.* **38**, 1151 (1967).

<sup>20</sup> The  $4d$  ion Zr result should not be compared in detail with the others. The  $4d$  core polarization is expected to be  $\sim -375 \text{ kG}/\mu_B$  [e.g., see R. E. Watson and A. J. Freeman, in *Hyperfine Interactions in Matter*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967), Chap. II] and the  $5s$  contact term is similarly larger than the  $4s$  counterpart(s) appropriate to the  $3d$  metals.

<sup>21</sup> G. W. West, *Phil. Mag.* **15**, 855 (1967).

<sup>22</sup> Temperature-dependent orbital terms have been proposed for Sc and La, transition metals of smaller  $n_e$  than those considered here. See Ref. 11.

plausible given the results of Figs. 3 and 5 for varying  $n_e$ . Let us consider this matter. The Pauli term involves the flipping of electron spins of states in the immediate vicinity of the Fermi energy. The thermal population and depopulation of (the same) states associated with the Fermi function leads<sup>23</sup> to the temperature dependence of the susceptibility. In contrast, the orbital term involves states throughout the bands (i.e., states both within and outside of  $\pm kT$  of  $E_F$ ) since it arises from the mixing of unoccupied Bloch-orbital character into the occupied one-electron states. Barring temperature-dependent orbital matrix elements, the term is temperature-dependent to the extent that states within  $\pm kT$  of  $E_F$  are important to the orbital mixing. While a strong temperature-dependent term might arise for a particular metal or alloy, one does not expect it to remain strong for changes in  $n_e$  corresponding (crudely) to shifting  $E_F$  through the bands by many times a typical  $kT$  value. Arguments such as this are regrettably inconclusive, particularly since we suggest that orbital terms are important to the temperature-independent part of the Knight shift. Attributing the major temperature dependence to the Pauli term appears *more plausible*. Both  $K$  and  $\chi$  follow the density of states suggested by the  $\gamma$  of Fig. 1 (suggesting the importance of the Pauli term to over-all behavior). Also, the  $s$  admixture, which will be obtained, is reasonable. Equation (1) will be assumed in what follows.

For lack of information as to the relative spin moments (and associated wave-function character) induced on Fe and Co sites due to the Pauli term, let us assume them the same. This is not essential and will likely have to be abandoned when more is known of the alloy system, but doing this, the Knight shift is given by

$$K = \{f_s\alpha_s + f_d\alpha_d\}\chi_{\text{Pauli}}(T) + f_{\text{VV}}\beta\chi_{\text{VV}}, \quad (2)$$

where

$$\alpha_s = \{\Omega/\mu_B\}H_{\text{hf}}(s)$$

and

$$\alpha_d = \{\Omega/\mu_B\}H_{\text{hf}}(d).$$

$H_{\text{hf}}(s)$  and  $H_{\text{hf}}(d)$  are the hyperfine fields associated with Co  $4s$  contact and  $3d$  core polarization hyperfine terms (taken to be  $+1700$  and  $-140$  kG/ $\mu_B$ , respectively) and  $\beta$  is the similar orbital hyperfine constant. In the tight-binding approximation,<sup>11</sup>  $\beta = 2\Omega\langle r^{-3} \rangle$ . (We will employ a Co  $\langle r^{-3} \rangle$  value<sup>24</sup> of 4.79 a.u.) In first approximation,  $f_s$  and  $f_d$  are taken to be the fractions of  $s$  and  $d$  Fe-Co site (probability density) character associated with the band states at  $E_F$ . Actually, they

are *weighted* samplings of these fractions. The weighting involves any variation in orbital character, and in turn of  $\chi_{\text{Pauli}}$  and Knight-shift contributions (with respect to one another), of the Fermi surface states. It is traditionally assumed that parameters such as  $f_s$  and  $f_d$  are the actual fractional weights of band character. The orbital term's fraction of Co character  $f_{\text{VV}}$  is of course, *differently weighted*. Given the strong tendency of Co to display orbital effects, one would expect  $f_{\text{VV}}$  to be somewhat larger than the fraction predicted by a simple sampling of Co band character.

Assuming values of  $\alpha_s$ ,  $\alpha_d$  and  $f_s + f_d (= F)$ , the slopes of Fig. 5 readily yield values of  $f_s$ . Neutron diffraction results<sup>25</sup> for one of the ferromagnetic alloys indicate that approximately one fifth of the magnetization resides on the Ti sites. This would imply  $F \sim 0.8$  if one assumes common band character for the range of alloys of interest here. Normalized results for  $F = 0.5, 0.75$ , and 1.0 appear in Fig. 6 suggesting that the Co  $s$  character is of the order of 5% of the total Co  $s$  and  $d$  character for the Fe-rich alloys and between 11 and 15% at the Co-rich end. These results (which should be compared with the remaining  $f_d$ ) are of eminently reasonable magnitude for  $0.7 \leq F \leq 1.0$ . Two observations must be made concerning the assumptions underlying these results. First, the presence of any temperature-dependent orbital term would mean that the  $f_s$  values are overestimates. Secondly, and of more interest, we have assumed that identical spin moments are induced on Co and Fe sites. Any deviation from this could severely affect the Fe-rich alloy results but would hardly modify the results at the Co end. The tendency for  $f_s$  to decrease as  $x$  goes from 0.8 to 1.0 holds whether the induced Fe site spin is much larger than the Co or zero valued.

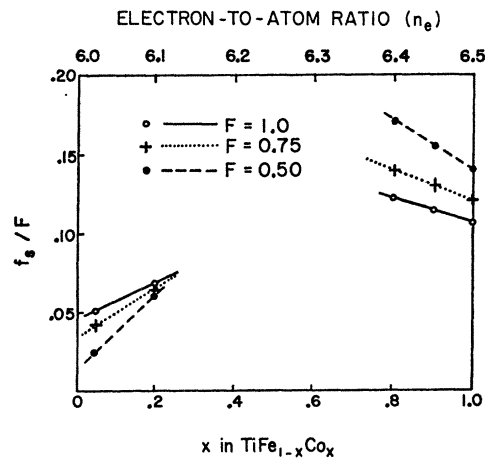


FIG. 6. The normalized  $s$  admixture fraction  $f_s/F$  as a function of  $x$  or  $n_e$  in the five alloys of  $\text{TiFe}_{1-x}\text{Co}_x$ , obtained from the  $K$  versus  $\chi$  diagram analysis.

<sup>23</sup> In simplest approximations,  $\chi_{\text{Pauli}}$  samples the densities of states at  $E_F$  and its temperature dependence the derivatives of the densities of states (with respect to energy). See Mott and Jones, Ref. 15.

<sup>24</sup> A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA.

<sup>25</sup> S. J. Pickart, Symposium on TiNi and Associated Compounds, Naval Ordnance Laboratory, 1967 (unpublished).

The varying  $s$  admixture is partially responsible for the remarkable resemblance between the room-temperature  $K$  versus  $n_e$  results shown in Fig. 3 and the  $\gamma$  versus  $n_e$  curve in Fig. 1. As a first approximation, one might expect  $\chi$  versus  $n_e$  to resemble  $\gamma$  versus  $n_e$ , and, therefore, if the orbital contribution remained constant, a close similarity between  $K$  versus  $n_e$  and  $\gamma$  versus  $n_e$  would result, according to Eq. (2), when  $\alpha_s f_s + \alpha_d f_d$  is positive and constant. The variation in orbital contribution to  $K$ , apparent in Fig. 5, is partially compensated by the variation in  $s$  admixture, causing  $K$  versus  $n_e$  to resemble  $\gamma$  versus  $n_e$  more closely than might be otherwise expected. The resemblance breaks down for the Fe-rich alloys where  $K$  is approximately constant while  $\gamma$  is increasing with electron concentration. This is probably because, with the small value of  $\gamma$  in this region, any variation of the orbital term dominates. We might note that the results of Fig. 6 appear similar to the density-of-states behavior suggested by Fig. 1. This is undoubtedly accidental.

$K$  has not always been found to vary with  $n_e$  so as to follow the electron-specific heat curve. For example, it was found<sup>26,27</sup> that the  $^{51}\text{V}$  Knight shift in V-Cr alloys increased slightly between V ( $n_e=5.0$ ) and V 60% Cr ( $n_e=5.6$ ) although  $\gamma$  is falling in this region, as shown in Fig. 1. At 60% Cr, the  $^{51}\text{V}$  Knight shift versus composition reverses slope and decreases, following the density-of-states curve. Although orbital effects are undoubtedly important<sup>28</sup> to the Knight shift in this region, present results suggest that varying  $s$  admixture may cause  $\alpha_s f_s + \alpha_d f_d$  to change sign for the V-Cr system by  $n_e=5.6$ , thereby causing the trend of  $K$  versus  $n_e$  to reverse itself and follow more closely to  $\gamma$  versus the electron-to-atom ratio.

It is instructive to apply the graphical  $K$  versus  $\chi$  analysis of Clogston and Jaccarino to the results. Assuming that only a temperature-independent orbital and a temperature-dependent Pauli term are of any significance, one simply plots the orbital term and determines its intercept with the observed curves. This is done for  $f_{\text{V}}$  values of 1.0 and 0.75 (the range seeming most reasonable) in Fig. 5, and the results suggest that the two terms are of approximately equal experimental importance. The positive slopes of the Co rich  $dK/d\chi$  curves, taken with the uncertainty in the slope of the Van Vleck term make detailed quantitative results unattainable. More important than this for all the results is the uncertainty in the zero of the Knight shift. Due to the strong tendency of Co to have orbital effects, one does not have a "safe" diamagnetic shift result<sup>29</sup> to set the zero. The  $x=0.2$  and 0.05 results help set a bound on the uncertainty in one

direction since we do not expect the temperature-independent component of the Knight shift to be negative. This suggests that the zero of the Knight shift could not be low by more than 1%<sup>30</sup> and, since we do expect some orbital contributions for these alloys, that it would be low by much less than this. We should further note that the assertion that the  $x=0.2$  and 0.05 intercepts should be positive implies (1) that orbital terms are important to the Co-rich Knight shifts and (2) that the orbital term does not dominate the temperature dependence (this relies on observing the higher intercepts which occur at the Co-rich end).

The Knight-shift results may also have bearing on the unusual absence of a hyperfine field in the Mössbauer effect<sup>3</sup> at the  $^{57}\text{Fe}$  site in the ferromagnetic state. The hf field per spin at the Co site appears to be positive for alloys near TiCo and negative near TiFe. One expects it to be near zero in the region where ferromagnetism appears ( $0.3 \leq x \leq 0.7$ ) and this, taken with the fact that we expect weaker orbital effects at an iron site, suggests that the absence of a hyperfine field may be at least partially due to a cancellation of terms. While acknowledging this possibility, it was earlier suggested that this behavior was due to a significant moment residing at the Ti site. Pickart's neutron-diffraction results,<sup>25</sup> placing most of the moment at the Fe-Co type site, suggest that this is only a part of the answer. Besides the cancellation of terms suggested by the  $^{59}\text{Co}$   $dK/d\chi$  results, there is influence of a possible distribution of hyperfine fields. The structure observed in the  $^{59}\text{Co}$  magnetic resonance line shows that the hyperfine field is influenced by the local next-nearest-neighbor environment and hence is certainly not homogeneous. An inhomogeneous magnetic field could be more easily obscured within the observed Mössbauer line.

It is planned to do Fe NMR with enriched samples. This will hopefully help resolve relative Fe and Co site behavior and in turn, a number of the uncertainties encountered above.

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<sup>27</sup> D. O. Van Ostenburg, D. J. Lam, H. D. Trapp, and D. E. Macleod, Phys. Rev. **128**, 1550 (1962).

<sup>28</sup> J. Butterworth, Proc. Phys. Soc. (London) **83**, 71 (1964).

<sup>29</sup> We use the most recent value of 1.0054 kHz/G suggested for  $^{59}\text{Co}$  by R. E. Walstedt, J. H. Wernick, and V. Jaccarino, Phys. Rev. **162**, 301 (1967).

<sup>30</sup> Or  $\frac{1}{2}\%$  if previously accepted value of 1.0103 kHz/G is used.