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Mössbauer-Effect Study of the Laves Phases $(Fe_{1-x}Mn_x)_2Ti$

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The Mössbauer spectra of a series of Laves phases $(Fe_{1-x}Mn_x)_2Ti$ have been measured at 77 and 300 °K. The results have been interpreted in terms of a two-site model, representing the two inequivalent positions for Fe atoms in the unit cell. This analysis indicates that Fe and Mn do not substitute randomly into the two sites. The variation of the isomer shift with composition is not adequately described by scaling the electronic charge density with volume.

I. INTRODUCTION

The intermetallic compounds Fe_2Ti and Mn_2Ti have the hexagonal structure characteristic of $MgZn_2$ (*C* 14). The lattice constants of these compounds have been reported previously.[1,2] The lattice parameters *a*, *c*, and the ratio *c*/*a* were found to be very nearly equal, in agreement with the notion that Fe and Mn have very similar electronic sizes. Because of this similarity, a complete solid solution of $(Fe_{1-x}Mn_x)_2Ti$ alloys can easily be obtained. In this work, a Mössbauer study of this pseudobinary system was performed. There are several reasons for studying this system. The magnetic properties of the cubic Laves phases containing iron and rare earths have been extensively studied by the use of the Mössbauer effect.[3-5] In almost all these compounds it was found that the magnetic hyperfine field at the Fe nucleus is approximately the same (230 ± 5) kOe despite the wide variety of environments studied. The isomer shift of Fe^{57} in a number of ordered XFe_2 Laves phases (X being in most cases a rare-earth element) was measured by Nevitt *et al.*,[6] who inferred from their data that the X component exerts no first-order effect on the isomer shift except through its constraint on the volume available to the iron atom. This finding is interesting and somewhat unexpected. It was felt that a Mössbauer study of an alloy system $(Fe_{1-x}Mn_x)_2Ti$ might help to clarify some of the earlier work on various Laves phases, since Fe_2Ti and Mn_2Ti are completely soluble in each other. If the simple picture of isomer shift depending only on atomic volume is adequate, one might expect a smooth monotonic change in isomer shift over the entire range of compositions. In addition, measurement on the compound Fe_2Ti should be useful since conflicting results for hyperfine field and quadrupole splitting have been reported previously.[3,6,7]

Kimball *et al.*[8] have studied the Mössbauer effect of Fe in the α-Mn structure (0–30 at.% Fe). In this complicated structure there are 58 atoms per unit cell, occupying four crystallographically inequivalent positions. Two of the sites have much larger coordination numbers (CN 16) than the other two (CN 12, CN 13). On the basis of a size effect, it was argued that the smaller Fe atoms fill mainly the lower coordination sites. In the Fe_2Ti structure, the coordination number for both sites is 12. The interatomic distances for the two sites are also close. Therefore, it is reasonable to expect that no appreciable size effect will be observed in the $(Fe_{1-x}Mn_x)_2Ti$ alloys. Kimball *et al.* also showed that Fe and Mn produce almost identical effects at a neighboring nucleus. Consequently, very little change in the isomer shift or quadrupole splitting with composition was observed, and narrow linewidths were found. The $(Fe_{1-x}Mn_x)_2Ti$ system should be a suitable system to test the notion that Fe and Mn are electronically similar. The advantages are that this system involves little size effect and has a wide range of compositions. In addition, the magnetic properties of this system should be quite interesting. Magnetic ordering has been observed in Fe_2Ti at low temperature, and from Mössbauer-effect measurements it appears that one site for Fe is quite different from the other magnetically.[3] A composition-dependent ferromagnetic to antiferromagnetic transition has been observed[9,10] in Fe_2Ti with deviation from stoichiometry. Mössbauer-effect study of this system can yield valuable information on any preference in filling the two magnetically distinct sites as Fe is replaced by Mn. This kind of information should be useful in interpreting the magnetic susceptibility of these alloys.

II. EXPERIMENTAL PROCEDURE

The alloys used as powdered absorbers in these experiments were prepared by induction melting of the appropriate quantities of Fe(99.99% pure), Mn(99.99% pure), and iodide Ti. During the melting process a certain amount of Mn evaporated from the sample. This was compensated for by adding extra Mn to the initial components. After melting, the ingot was carefully weighed to ensure that the composition was close to the nominal one. After annealing for approximately 2 days at 800 °C, the samples were examined by x-ray analysis and determined to have the Laves structure $MgZn_2$. The lattice parameters for the alloys are shown in Fig. 1. For the Mössbauer experiments, a standard spectrometer[11] operating in the constant acceleration mode was used. The source was Co^{57} in Cu. In the low-temperature experiments, both source and absorber were cooled.

III. RESULTS AND DISCUSSION

A. Room Temperature

Mössbauer absorption spectra at room temperature (300 °K) for the $(Fe_{1-x}Mn_x)_2Ti$ alloys are shown in Fig. 2. It can be seen that as the Mn concentration is increased, the character of the spectrum gradually changes into what appears to be an asymmetrical quadrupole doublet. For lower Fe concentration, the appearance of a second quadrupole component becomes evident.

To further investigate the "asymmetry" of some of the spectra, a few of the samples showing the largest effect were investigated over a wide range of temperatures (77–700 °K). If the asymmetry were the result of an anisotropic Debye-Waller factor, or Goldanskii effect,[12] then it should become more pronounced as the temperature is increased. However, the absorption spectrum changed very little with temperature and definitely showed no increase in asymmetry. Representative results for $(Fe_{0.5}Mn_{0.5})_2Ti$ are shown in Fig. 3. Relaxation effects were also considered as possible cause for the asymmetry,[13] but the lack of any appreciable variation with temperature made this possibility unlikely.

An alternative explanation not excluded by the temperature dependence of the spectra is based on the fact that the unit cell of Fe_2Ti has two crystallographically inequivalent sites. In this structure (space group $P6_3/mm^3$) there are eight Fe atoms per unit cell, two in the $2a$ position (Fe_I) with point symmetry $3\bar{m}$, and six in $6h$ position (Fe_{II}) with symmetry $mm\bar{m}$.[2] As Mn is substituted for Fe in the Fe_2Ti lattice, the parameters associated with each site may vary in a different way. In particular, the isomer shifts for Fe atoms in the two sites must begin to differ significantly in order to produce a spectrum which is not symmetrical. Slightly different quadrupole splittings or linewidths would tend only to broaden the doublet if the isomer shifts remained the same.

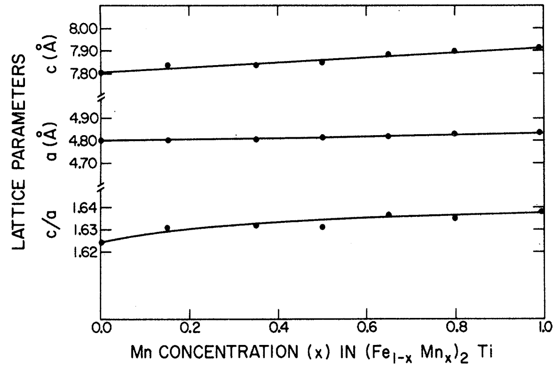

FIG. 1. Lattice parameters of the $(Fe_{1-x}Mn_x)_2Ti$ alloys.

In this investigation the spectra were all fitted using this two-site model for the alloys, and as can be seen from Fig. 2, the agreement with experimental data is very good. Of course, a two-site fitting is merely an approximation for any of the alloys (except the compound Fe_2Ti), because of the many possibilities for nearest-neighbor configurations. In general, one would expect that this model might be valid only at the extreme ends of the composition range. However, in the case of the alloys studied here, the electronic similarity of Fe and Mn make this model quite reasonable. In this study, as well as in that of Kimball *et al.*,[8] it seems that the effects of Fe or Mn atoms at neighboring Fe nuclei are almost identical, as will be described in detail later. Thus the many components of the absorption spectrum can be well approximated by just two components representing the two sites for Fe atoms in the unit cell. The narrow linewidths found in this model are further justification for its use. For site I, a linewidth of approximately 0.22 mm/sec was found for all the alloys. For site II, values in the range 0.26–0.30 mm/sec were found, the larger values occurring in the alloys approaching Fe_2Ti. Besides the broadening due to alloying effects in these alloys, there may be some broadening due to magnetic interactions. The compound Fe_2Ti, for example, becomes antiferromagnetic[3] just below room temperature (T_N = 279 °K).

The parameters obtained by a least-squares fitting procedure are shown in Figs. 4–6. Lorentzian line shapes were assumed. Figure 6 shows the relative intensity of two doublets, defined as the ratio of their areas. The area under each doublet is directly proportional to the product of the average number of Fe atoms in that site and the corresponding probability of recoilless absorption. In the Debye model, the latter is a function only of (T/Θ_D). For $T \ll \Theta_D$,

$$f = \exp\left[-\frac{3}{2}\frac{E_R}{k\Theta_D}\left(1+\frac{2\pi^2}{3}\frac{T^2}{\Theta_D^2}\right)\right], \qquad (1)$$

where E_R is the recoil energy associated with the

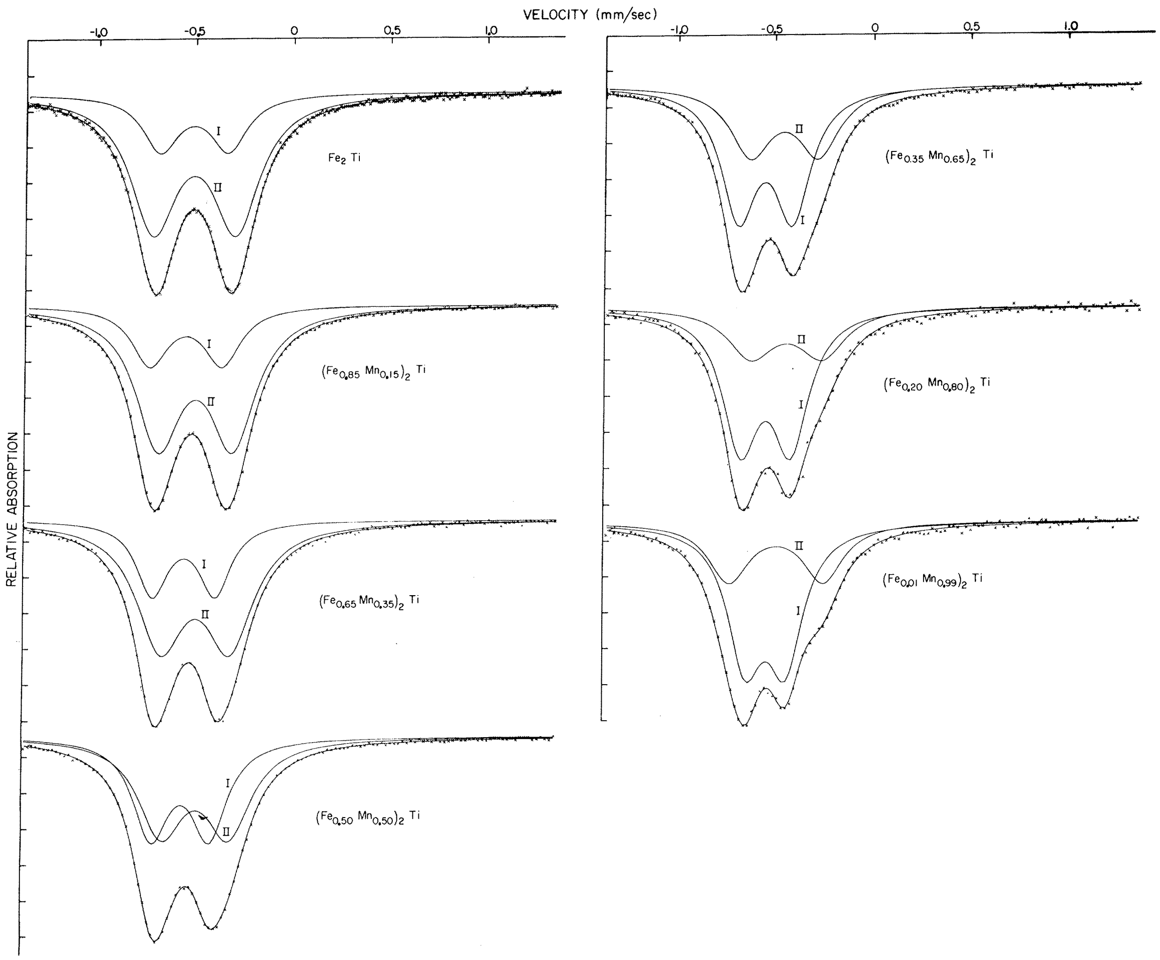

FIG. 2. Mössbauer spectra of the $(Fe_{1-x}Mn_x)_2Ti$ alloys at room temperature (300 °K).

transition.[14] Assuming for a moment that this probability or f factor is the same for both sites, it can be seen from Fig. 6 that in the low Fe concentration alloys there is a definite preference of Fe atoms for site I. If Fe atoms substituted randomly into the lattice, then the area ratio would be 3:1, independent of composition, since site II has six positions and site I only two. From the curve in Fig. 6 the probability that site I or site II is occupied by an Fe atom can be calculated. It is clear that at low Fe concentration the Fe atoms have a strong preference for site I. The assumption of equal Debye temperature for the two sites would imply that the area ratio should be independent of temperature, within the framework of the Debye approximation. Since the Debye temperature appears in the exponent in the expression for the recoilless fraction, a small difference in Debye temperatures for the two sites would cause quite a large variation of the relative intensity with temperature. Low-temperature results (Fig. 7) for the area ratio show that, in fact, there is little temperature dependence. Thus it is justified to assume equal recoilless fractions for the two sites.

Given the preferential filling of site I shown in Fig. 6, one might hope that this effect can be explained, at least partially, in terms of a size effect, with the smaller Fe atoms favoring the site with the smaller atomic volume. Table I lists the interatomic distances in the Fe_2Ti structure. Since the atomic radii of Mn and Fe are very close and the interatomic distances for site I and site II are almost the same, it is difficult to explain the relative intensity solely on this basis.

The isomer shift data of Fig. 4 can be explained in terms of two contributions to the change in electronic density at the nucleus. First there is an effect due to the changing atomic volume experienced by an Fe atom as the concentration varies. Since the isomer shift can be written[15]

$$\mathcal{S} = \frac{4\pi Z^2 e^2}{5} R^2 \frac{\Delta R}{R} [\, |\Psi_A(0)|^2 - |\Psi_S(0)|^2 \,] \,, \qquad (2)$$

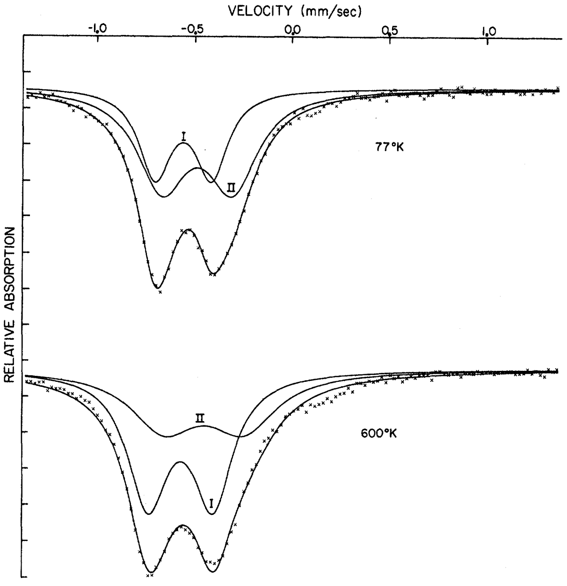

FIG. 3. Absorption spectrum of $(Fe_{0.5}Mn_{0.5})_2Ti$ at two different temperatures.

with negative $\Delta R/R$ for Fe, an increase in electronic density at the nucleus in an absorber will produce a decrease in isomer shift. In pressure experiments with pure Fe, Pound[16] and others[17,18] have found that the 4*s* electron density at the nucleus varies approximately according to the relation

$$\frac{\Delta \mathcal{I}}{\Delta(V/V_0)} = 1.4 \text{ mm/sec} , \qquad (3)$$

where $\Delta(V/V_0)$ is the fractional change in volume of a unit cell. For more closely packed structures, however, it was found that the *s* electron density changes less rapidly. In the high pressure hcp phase of Fe, there is very little dependence of isomer shift on lattice parameter.[17] Nevitt *et al.*[6] have found that the isomer shift of Fe in various ordered Laves phases can be accounted for in terms of the changing atomic volume. Little dependence on the nature of the other component was seen. From the lattice parameter data of Fig. 1, it is evident that a contribution from the volume effect will lead to a continuous increase in isomer shift from Fe_2Ti to Mn_2Ti, since there is an increase of approximately 3% in the volume of a unit cell.

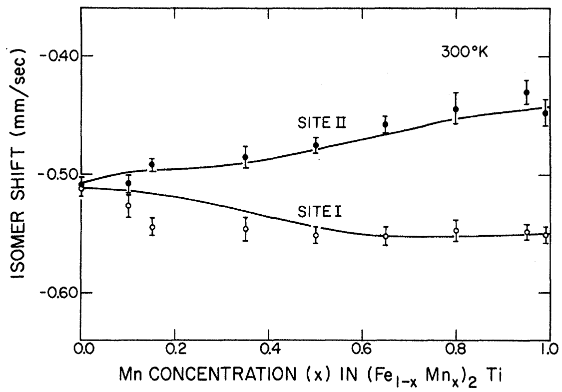

FIG. 4. Composition dependence of the isomer shift at room temperature. Solid curves are calculated as described in the text.

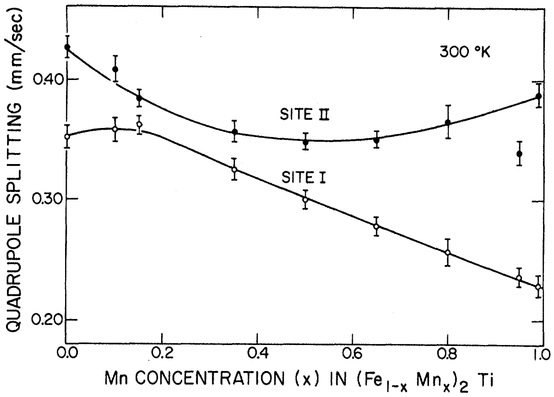

FIG. 5. Composition dependence of the quadrupole splitting at room temperature.

Another contribution to the isomer shift comes from what might be called a band structure, or electron concentration effect. If we adopt a rigid band model for the $(Fe_{1-x}Mn_x)_2Ti$ alloys, we expect that just as for most transition metals, there will be one broad band arising from the 4*s* electrons, and another, much narrower, coming from the 3*d* electrons. The change in electron concentration will then result in a lowering of the Fermi level with increasing Mn, the number of 3*d* electrons affected being much greater than that of 4*s* electrons since the density of states in the 3*d* band is expected to be much larger. If this reflects itself locally at an Fe atom, the shielding by the 3*d* electrons of the 3*s* and 4*s* electrons should be less. Therefore, the *s* electron density at the nucleus will increase and the isomer shift decrease with increasing Mn. If we assume that the greatest change is for the 3*s* electrons, then the net change in isomer shift can be broken into two separate terms: a volume term and a shielding term.

It has been found in many cases[19] that at least over a limited range of compositions there is an approximate linear dependence between the isomer shift and the number of Fe nearest neighbors. From the above discussion, an increase in Fe neighbors should lead to an increase in isomer shift. In attempting to approximate this effect and the volume effect we may write

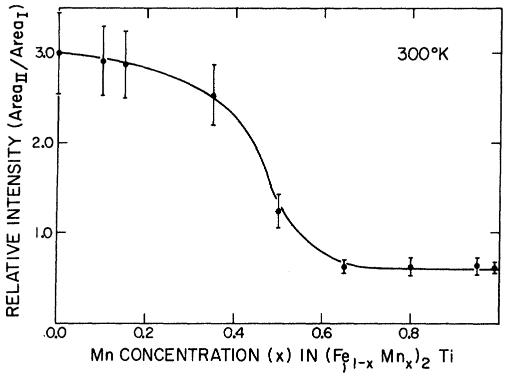

FIG. 6. Composition dependence of the relative intensity of the two doublets at room temperature.

$$\mathcal{I}_{\mathrm{I}} = \mathcal{I}_{\mathrm{I}}(0\%\mathrm{Fe}) + \alpha_1 N_{\mathrm{I}}^{\mathrm{II}} + \beta_1 \Delta V/V, \tag{4}$$

$$\mathcal{I}_{\mathrm{II}} = \mathcal{I}_{\mathrm{II}}(0\%\mathrm{Fe}) + \alpha_2 N_{\mathrm{II}}^{\mathrm{I}} + \alpha_3 N_{\mathrm{II}}^{\mathrm{II}} + \beta_2 \Delta V/V, \tag{5}$$

where $N_{\mathrm{I}}^{\mathrm{II}}$ is the average number of $\mathrm{Fe_{II}}$ neighbors for $\mathrm{Fe_I}$ (as determined from Fig. 6), $\Delta V/V$ is the fractional change in volume from Mn_2Ti (0%Fe), and α_1, α_2, α_3, β_1, and β_2 are constants which may depend on composition. Such equations have been found to adequately describe the effects of pressure on the isomer shift on Fe in many hosts[17,18] and the change in isomer shift for dilute impurities in Fe.[19] Since in the present alloy system there is a wide range of compositions, Eqs. (4) and (5) may not be valid over the entire range. However, as a first approximation, it was assumed that Eqs. (3) and (4) held over the entire range. The isomer shifts calculated from Eqs. (4) and (5) and using $\alpha_1 = \alpha_2 = \alpha_3 = 0.015$ mm/sec, $\beta_1 = 1.8$ mm/sec, and $\beta_2 = 5.6$ mm/sec are shown as solid lines in Fig. 4. The agreement between the theoretical curve and experimental points is reasonable, in view of the fact that a simple theoretical model was used. The important point, however, is that the isomer shift data cannot be explained by merely scaling the charge density with atomic volume. If this were an adequate description, the isomer shift would be continuously increasing from Fe_2Ti to Mn_2Ti. This is approximately true for site II, but not for site I. It is clear that the local environment of a given Fe atom also plays a role in determining the isomer shift.

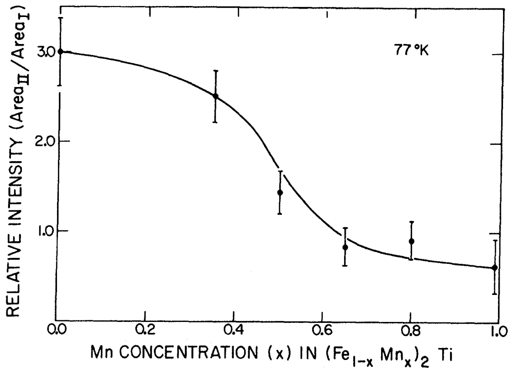

FIG. 7. Composition dependence of the relative intensity of the two doublets at liquid-nitrogen temperature.

B. Low-Temperature Results

The Mössbauer spectra of the $(Fe_{1-x}Mn_x)_2Ti$ alloys at liquid-nitrogen temperature (77 °K) were virtually identical with those at room temperature, with the exception of Fe_2Ti and $(Fe_{0.85}Mn_{0.15})_2Ti$. In these two alloys, there is a noticeable magnetic hyperfine splitting (Fig. 8). The analysis, made on the basis of a two-site model previously described, produced good agreement in all cases except $(Fe_{0.85}Mn_{0.15})_2Ti$. In this alloy, at 77 °K, there appears to be more than one hyperfine field at the Fe nuclei, since a simple two-site model was inadequate to fit the data. Such nonunique hyperfine fields could arise because of different nearest-neighbor configurations. An attempt to fit the observed spectrum with two distinct values for hyperfine field at site II is shown in Fig. 8. For Fe_2Ti, the fitting was obtained by assuming a hyperfine field at the $\mathrm{Fe_{II}}$ sites, but none at the $\mathrm{Fe_I}$ sites. This agrees with an earlier result of Wallace,[3] but our value of 94 kOe for the hyperfine field is in substantial disagreement with his result of 71 kOe. Furthermore, the quadrupole splitting reported here is twice that of Wallace. Both of these results substantiate those of Nevitt *et al.*,[6] who also noted a disagreement of their data on Fe_2Ti with those of Ref. 3.

The isomer shift and quadrupole splitting obtained were very close to their room-temperature values, and are not shown. There is no significant temperature variation of the isomer shift due to the second-order Doppler effect because both source and absorber are at the same temperature. The ratio of the two doublets is shown in Fig. 7. To obtain accurate values for the area ratio in the low

TABLE I. Distances of neighbor atoms for the two Fe sites in the Fe_2Ti structure.

Site	Neighbors	Distance (Å)
$\mathrm{Fe_I}$	6 $\mathrm{Fe_{II}}$	2.40
	6 Ti	2.81
$\mathrm{Fe_{II}}$	2 $\mathrm{Fe_I}$	2.39
	2 $\mathrm{Fe_{II}}$	2.40
	2 $\mathrm{Fe_{II}}$	2.40
	2 Ti	2.80
	4 Ti	2.81

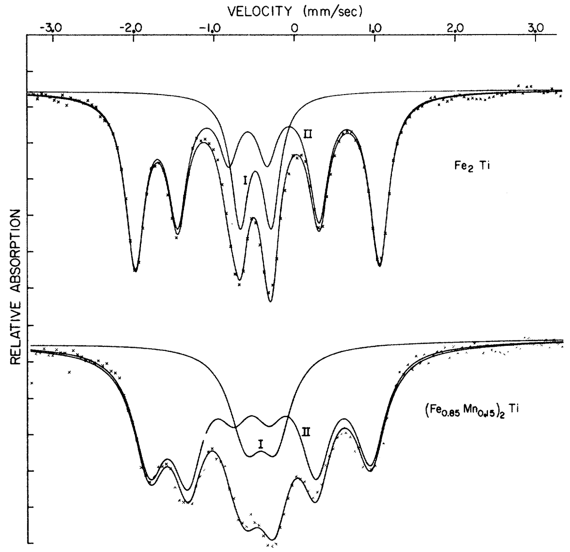

FIG. 8. Mössbauer spectra for the two alloys which show magnetic hyperfine splitting at 77 °K.

Fe concentration samples it was necessary to take into account absorption by the Fe impurities in the Be windows of the Dewar and counter tube. In two cases this changed the area ratio appreciably. The small discrepancy between the room-temperature and the liquid-nitrogen temperature relative intensities for these samples may result from the method of correction.

IV. CONCLUSIONS

The Mössbauer effect has been used to study the Laves phases $(Fe_{1-x}Mn_x)_2Ti$ by using a two-site model representing the two inequivalent Fe sites in the Fe_2Ti unit cell to interpret the results. A somewhat surprising preference for site I by Fe atoms was found at low Fe concentration. A small but systematic change in all the parameters was observed as the composition varied over the whole range. In their study of the α-Mn–Fe system Kimball *et al.*[8] observed no systematic changes in isomer shift, etc., but noted that all parameters were relatively constant over a concentration range 0–30% Fe. From the study of the $(Fe_{1-x}Mn_x)_2Ti$ system we can also conclude that the effect of a neighboring Mn atom is approximately the same as that of Fe atom, the difference in isomer shift being perhaps 0.01 mm/sec.

The isomer shift variation with composition is not entirely explained on the basis of a changing atomic volume, although this factor should be considered. The fact that earlier results[6] had success with this simple approach may be due to two distinct causes: (a) The associated changes in isomer shift in going from one compound to another were much greater, and the trend was evaluated on a grosser scale. (b) In the XFe_2 Laves phases in many or even most cases the X component was a rare earth. In this case there may really be little interaction between the 3*d* electrons of Fe and the more localized 4*f* electrons of the rare earth. This is borne out in part by the fact that in most of these compounds, the hyperfine field at the Fe nucleus is about (230 ± 5) kOe, almost independent of the X component. In the $(Fe_{1-x}Mn_x)_2Ti$ system, however, the low-temperature results indicate that there must be a strong influence on the magnetic properties when Mn is substituted for Fe into the Fe_2Ti lattice.

Two possibilities for further research are suggested from the present results. It would be interesting to study the magnetic susceptibility of the alloys in light of the preferential occupancy of site I by Fe. This knowledge could be helpful in view of the fact that the two sites in the Fe_2Ti are quite different magnetically, as verified by the low-temperature Mössbauer spectrum. Secondly, a neutron diffraction study of the $(Fe_{1-x}Mn_x)_2Ti$ alloy should be capable of confirming the filling determined here, since Fe and Mn have greatly different scattering cross sections for neutrons.

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Microwave-Optical Double Resonance of the Metastable $4f^6 5d$ Level of Eu^{2+} in the Fluorite Lattices

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The results of an electron-spin-resonance investigation of the metastable $4f^6 5d$ level of Eu^{2+} in CaF_2, SrF_2, and BaF_2 are presented. The experiments utilized the intense fluorescence from the lowest-lying $\Gamma_8(4f^6 5d)$ level of Eu^{2+} to the ${}^8S_{7/2}(4f^7)$ ground state for the optical detection of resonance transitions in the excited state. The magnitudes of the Zeeman and hyperfine splittings for the excited state are consistent with the model of a large crystal-field splitting for the $5d$ electron and a considerably smaller coupling of this electron to the $4f^6$ configuration. The large average g value of 3.80 for this level can be explained by an effective exchange coupling between the $5d$ spin and the $4f^6({}^7F_J)$ spin component if this coupling is comparable to the 400-cm^{-1} spin-orbit coupling parameter for the ${}^7F_J$ multiplets. The anomalous line shapes of the resonance spectrum can be interpreted on the basis of a dynamical Jahn-Teller distortion of the e_g orbital of the $5d$ electron. A singlet tunneling level associated with the Jahn-Teller effect is estimated to be at about 10 cm^{-1} above the orbital doublet Γ_8 level in both SrF_2 and CaF_2 on the basis of the line shapes observed in the resonance spectrum. Previously unidentified optical transitions to these levels have been observed by other workers, who also measured the splitting of the Γ_8 level by uniaxial strains and the strain coupling of the singlet tunneling level to the Γ_8 level. These piezo-optic data are in quantitative agreement with the model of a dynamical Jahn-Teller interaction for the observed levels. The nature of the fluorescence spectrum of Eu^{2+} in BaF_2 is basically different from that observed for Eu^{2+} in CaF_2 or SrF_2. However, an optically detected resonance spectrum identical to that of CaF_2 or SrF_2 has been observed for Eu^{2+} in BaF_2.

I. INTRODUCTION

The divalent configurations of the lanthanide elements with incomplete $4f$ shells all have strong optical absorptions in crystalline environments, beginning in the visible region of the spectrum and extending into the ultraviolet.[1] The absorption results from the electric dipole allowed $4f^n \rightarrow 4f^{n-1}5d$ transitions, which are considerably phonon broadened in crystalline spectra as a result of the large crystal-field coupling of the $5d$ electron. The electron-lattice coupling in many crystals is of such a magnitude that sharp direct transitions as well as vibrational satellites and many-phonon bands are simultaneously observed in these spectra. This property has led to much experimental activity directed toward the understanding of the electronic structure and crystalline-field interactions of the $4f^{n-1}5d$ configurations. A large portion of this work has been done using the fluorite lattices CaF_2, SrF_2, and BaF_2 as hosts for the RE^{2+} ions because most elements of this series are relatively stable in these crystals.

We report here on the results of an electron-spin-resonance (ESR) investigation of the lowest $4f^6 5d$ level of the Eu^{2+} ion in these lattices. Our work supports the model of a crystal-field splitting for the $5d$ electron, which is considerably larger than the combined effects of the Coulomb coupling of this electron to the $4f^6$ "core" electrons and spin-orbit coupling. In addition, evidence is found for the existence of a dynamical Jahn-Teller distortion of the orbitally degenerate e_g component of the $5d$ electron. The effects of the Jahn-Teller coupling on the ESR spectra of this excited state have features in common with the recently reported spectra of