

significantly from the rms values which technically should be used. The equilibrium charge states were measured for Formvar and carbon stripping foils; comparisons between charge states in different media imply that these values should not differ measurably from those in Mylar.<sup>14</sup> The same qualitative discrepancy between effective and rms charge states was noted in Ref. 3 for Br and I ions in various foils, and for Cl ions in gold and aluminum foils in Ref. 4. In the latter work, the effective charges of O<sup>16</sup> ions were found to agree within experimental uncertainties with the rms charge values in gold and aluminum. We can, at present, offer no explanation for the large discrepancies between effective charge and actual charge. The obvious empirical statements are that the effective charge of Eq. (2) must at present be considered solely as a parameter, and the rms charge values may not be used with Eq. (2) to calculate  $(dE/dX)_e$  for heavy ions.

The correlation of Fig. (1) implies the possibility of computing heavy-ion  $dE/dX$  values by estimating an effective charge from Fig. 1 and substituting this value and proton stopping powers into Eq. (2). While

the correlation is good in the higher-velocity region of Fig. 1 for O<sup>16</sup>, S<sup>32</sup>, and Cl<sup>35</sup> ions, the Br<sup>79</sup> and I<sup>127</sup> data do not extend into this region. It would, therefore, be valuable to have stopping-power data for higher-energy bromine and iodine ions in order to extend the range of ions and velocities over which the curve of Fig. 1 may be used to calculate stopping powers. The curve of Fig. 1 is also consistent with the results of Heckman *et al.* for lighter heavy ions.<sup>16</sup>

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<sup>16</sup> H. H. Heckman, B. L. Perkins, W. G. Simon, F. M. Smith, and W. H. Barkas, *Phys. Rev.* **117**, 544 (1960).

## Mössbauer Studies of the SrTiO<sub>3</sub>:Fe<sup>57</sup> System

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Mössbauer studies of the SrTiO<sub>3</sub>:Fe<sup>57</sup> system used as an absorber have shown that iron enters the SrTiO<sub>3</sub> lattice substitutionally at the Ti<sup>4+</sup> site in its high-spin ferric state and is usually associated with a charge-compensating oxygen vacancy in agreement with the EPR evidence. On firing these samples in hydrogen, the quadrupole-split spectrum of Fe<sup>3+</sup> associated with an oxygen vacancy transforms into a Zeeman-split spectrum with hf field and isomer shift characteristic of iron metal, indicating the formation of colloidal iron. Vacuum firing of the original air-fired samples tends to convert part of the Fe<sup>3+</sup> ions into Fe<sup>2+</sup> through the creation of more oxygen vacancies. The stages through which atomically dispersed Fe<sup>3+</sup> ions are converted into colloidal iron on hydrogen firing and vice versa have been indicated.

### I. INTRODUCTION

THE EPR studies of Fe<sup>3+</sup> in SrTiO<sub>3</sub> reported by Müller<sup>1</sup> and Dobrov *et al.*<sup>2</sup> suggest that Fe enters the SrTiO<sub>3</sub> lattice at the Ti<sup>4+</sup> site in its high-spin ferric state without any vacancy association. These studies have been carried out with extremely low concentrations of iron. If, however, the concentration of iron is increased, there is a possibility for a charge-compensating oxygen vacancy to be associated with the probe, as is suggested by Mössbauer-effect (ME) studies of the BaTiO<sub>3</sub>:Fe<sup>57</sup> system.<sup>3</sup> Further, it has been shown by our earlier results that the valence state of a ME probe in a given lattice can be altered by giving any

of a variety of heat treatments to the system.<sup>4</sup> This paper reports the ME study of Fe-doped SrTiO<sub>3</sub> subjected to a variety of heat treatments. It is seen that for all the concentrations that are normally used in the ME studies, the Fe<sup>57</sup> probe in an air-fired SrTiO<sub>3</sub> system is associated with a charge-compensating oxygen vacancy. The reduction of the lattice by vacuum firing tends to stabilize the Fe<sup>2+</sup> state in addition to the usual Fe<sup>3+</sup> state. On firing the samples in hydrogen, however, colloids of iron have been detected, confirming once again that the electronic structure of the ME probe is dependent on the thermal treatment of the sample.

### II. EXPERIMENTAL: SAMPLE PREPARATION

Single crystals of SrTiO<sub>3</sub> grown by the Verneuil technique were obtained from the National Lead Co.<sup>5</sup>

<sup>1</sup> K. A. Müller, *Helv. Phys. Acta* **31**, 173 (1958).

<sup>2</sup> W. I. Dobrov, R. F. Vieth, and M. E. Browne, *Phys. Rev.* **115**, 79 (1959).

<sup>3</sup> V. G. Bhide and M. S. Multani, *Phys. Rev.* **149**, 289 (1966).

<sup>4</sup> V. G. Bhide and H. C. Bhasin, *Phys. Rev.* **159**, 586 (1967).

<sup>5</sup> A batch of the single crystals was given by the National Lead Co., New York.

These crystals were crushed and powdered to about 400 mesh. Required amounts of SrTiO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> enriched to 92% Fe<sup>57</sup> were taken and thoroughly mixed in an agate mortar with a small addition of alcohol. This mixture was then dried and pressed into pellets, and heated in air at 1100°C for nearly 12 h. The pellets were crushed, mixed, and pressed again, and then fired at 1200°C for another 12 h. After this firing schedule the pellets were crushed and the powder was compressed into disks with the optimum thickness for ME spectroscopy. That the solid-state reaction was complete, was tested by using the x-ray method. The ME spectra were obtained using a constant-velocity drive described earlier.<sup>6</sup>

### III. RESULTS AND DISCUSSION

In the investigation reported here, SrTiO<sub>3</sub> was doped with Fe<sup>57</sup>, and its Mössbauer spectra were taken under three distinct conditions of sample treatment. In the first, the samples were annealed in air at 1000°C for 3 h, and then they were matched against a Co<sup>57</sup>:Cu source to obtain Mössbauer spectra. The spectrum obtained with a sample containing 3-at.% iron is shown in Fig. 1(a). It clearly shows two distinct resonances, one at -0.4 mm/sec and the other at +0.6 mm/sec. Such a spectrum could be interpreted as due to two charge states or to the quadrupole interaction of a single charge state. The spectrum did not change appreciably,

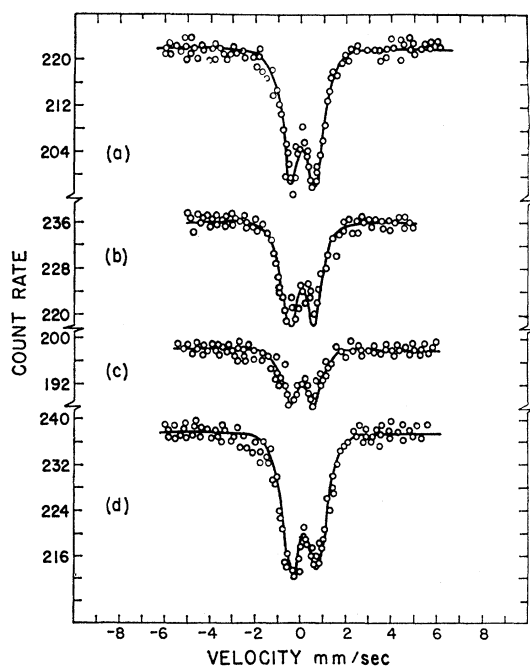


Fig. 1. Mössbauer spectra of the SrTiO<sub>3</sub>:Fe<sup>57</sup> system with various concentrations of iron: (a) 3.0 at.% (room temperature), (b) 1.5 at.% (room temperature), (c) 0.3 at.% (room temperature), and (d) 3 at.% (78°K).

<sup>6</sup> V. G. Bhide and M. S. Multani, Phys. Rev. **139**, A1983 (1965).

except for the temperature-dependent shift of the centroid of the spectrum, over the temperature range 78 to 500°K. The spectra for similarly fired 1.5-at.%- and 0.3-at.%-doped samples are shown in Figs. 1(b) and 1(c), respectively. These spectra are almost identical with that shown in Fig. 1(a). It is significant that the two peaks are of the same intensity in each of these spectra, whatever the concentration of iron or the sample temperature. These observations rule out the possibility of two charge states coexisting. Further, the peak positions do not conform with the isomer-shift systematics of different valence states of iron, while on the other hand, the position of the centroid of the spectrum at  $0.10 \pm 0.04$  mm/sec is characteristic of the high-spin ferric state.<sup>7</sup>

SrTiO<sub>3</sub> crystallizes in ideal perovskite structure, which is cubic at room temperature.<sup>8</sup> The EPR studies of Müller,<sup>1</sup> Dobrov *et al.*,<sup>2</sup> and Kirkpatrick *et al.*<sup>9</sup> are unambiguous in that Fe<sup>3+</sup> enters the SrTiO<sub>3</sub> lattice substitutionally at the Ti<sup>4+</sup> site in its high-spin ferric state. At low concentrations the Fe<sup>3+</sup> ion sees a perfect-lattice local environment, but if the concentration is increased (as in the experiment of Kirkpatrick *et al.*), then one observes an axial spectrum of Fe<sup>3+</sup>, due to an associated charge-compensating oxygen vacancy, along with the cubic spectrum. The axial spectrum is of course expected to dominate on increasing the iron concentration. Such vacancy association in heavily doped BaTiO<sub>3</sub> and PbTiO<sub>3</sub> has been reported by Gainon<sup>10,11</sup> from EPR studies, and by Nicholson and Burns<sup>12</sup> and by Bhide and Multani<sup>3</sup> from ME studies. These results suggest that the observed ME spectra can be interpreted as the quadrupole-split spectrum of Fe<sup>3+</sup> arising out of vacancy association. The observed quadrupole interaction,  $\Delta E = 1.00$  mm/sec, is also in fair agreement with that computed on the model of a point charge in the presence of a near-neighbor oxygen vacancy, which is 1.22 mm/sec.

One may perhaps argue that the quadrupole interaction observed in air-fired samples may be due to the existence of superparamagnetic particles of Fe<sub>2</sub>O<sub>3</sub> that have not reacted with the lattice. The quadrupole interaction for superparamagnetic Fe<sub>2</sub>O<sub>3</sub> particles with a size <100 Å is also of the same order as is experimentally observed.<sup>13</sup> But a little careful consideration will be enough to discard this possibility. In the first instance the quadrupole interaction for superparamagnetic Fe<sub>2</sub>O<sub>3</sub> is very dependent on particle size. Thus for Fe<sub>2</sub>O<sub>3</sub>, the quadrupole interaction is found to vary

<sup>7</sup> G. K. Wertheim, *Mössbauer Effect: Principle and Applications* (Academic Press Inc., New York, 1965), Chap. V.

<sup>8</sup> S. B. Levin, N. J. Field, F. M. Plock, and L. Merker, J. Opt. Soc. Am. **45**, 737 (1955).

<sup>9</sup> E. S. Kirkpatrick, K. A. Müller, and R. S. Rubins, Phys. Rev. **135**, A86 (1964).

<sup>10</sup> D. J. A. Gainon, J. Appl. Phys. **36**, 2325 (1965).

<sup>11</sup> D. J. A. Gainon, Phys. Rev. **134**, A1300 (1964).

<sup>12</sup> W. J. Nicholson and G. Burns, Phys. Rev. **129**, 2490 (1963).

<sup>13</sup> W. Kündig, H. Bömmel, G. Constabaris, and R. H. Lindquist, Phys. Rev. **142**, 327 (1966).

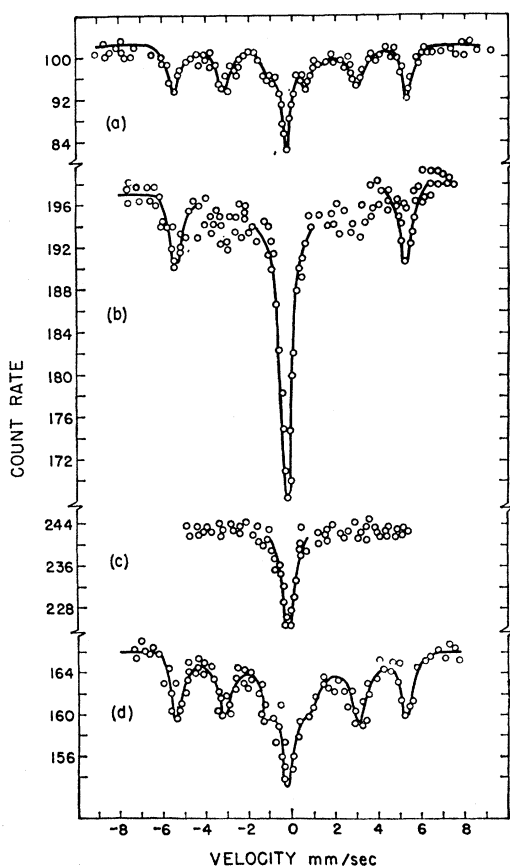


FIG. 2. Mössbauer spectra of  $\text{SrTiO}_3:\text{Fe}^{57}$  system with various concentrations of iron, fired in hydrogen at  $1000^\circ\text{C}$  for 2 h. (a) 3.0 at.%, (room temperature), (b) 1.5 at.%, (room temperature), (c) 0.3 at.%, (room temperature), and (d) 3 at.%, ( $78^\circ\text{K}$ ).

from  $0.98 \pm 0.001$  to  $0.44 \pm 0.03$  mm/sec as the particle size changes from  $<100$  to  $180 \text{ \AA}$ . The constancy of the quadrupole splitting in our experiments on air-fired Fe-doped  $\text{SrTiO}_3$  samples for all concentrations and over the temperature range 78 to  $500^\circ\text{K}$  shows unequivocally that the quadrupole interaction is not rooted in superparamagnetism. Furthermore, our magnetic susceptibility data show that the samples do not exhibit superparamagnetism. All these considerations seem to suggest that the observed ME spectrum for the air-fired sample is the quadrupole-split spectrum of  $\text{Fe}^{3+}$  at a  $\text{Ti}^{4+}$  site in the lattice with an associated oxygen vacancy.

These samples were then annealed in hydrogen atmosphere for 2 h at  $1000^\circ\text{C}$ . The spectra obtained with all three samples are shown in Fig. 2. Figure 2(a) shows a well-resolved Zeeman-split spectrum with a hf field of 330 kOe at room temperature and an isomer shift of  $-0.2 \pm 0.04$  mm/sec. In addition to the Zeeman-split spectrum there is a single line, positioned at about  $-0.3 \pm 0.04$  mm/sec. On cooling the sample down to  $78^\circ\text{K}$ , hardly any change in the spectrum is observed [Fig. 2(d)]. The single line remains at the same posi-

tion except for the temperature shift. On heating these hydrogen-fired samples with a small trickle of hydrogen flowing through the furnace, it was found that the Zeeman-split spectrum gradually collapses and disappears at a temperature that nearly corresponds to the Curie temperature of iron. With lower concentration samples (viz., 1.5 and 0.3 at.%) the spectra again show [Figs. 2(b) and 2(c)] the Zeeman-split spectrum and an additional line whose characteristics are identical, except for the fact that as the concentration is reduced the intensity of the Zeeman-split spectrum decreases, whereas the intensity of the single line increases. Indeed, for extremely low concentration, the Zeeman-split spectrum is barely detectable. The above observations clearly indicate that when Fe-doped  $\text{SrTiO}_3$  samples are heated in hydrogen, metallic iron colloids are formed. Such metallic colloids have been reported to be formed in many systems, particularly alkali halides, silver halides, etc.<sup>14</sup> Colloid centers of foreign impurities like Pb<sup>15</sup> and Cu<sup>16</sup> have also been detected in these lattices. Although these colloids almost certainly arise from an association of  $F$  centers to form large agglomerates, the process of agglomeration is not well understood. The complexity of the situation is evidenced by the recent observation that hydroxyl ions act as a catalyst for the formation of colloids.<sup>17,18</sup> Davidge<sup>19</sup> has also observed the formation of Fe colloids in an Fe-doped  $\text{MgO}$  lattice on hydrogen firing. We feel that the formation of colloidal iron in an Fe-doped  $\text{SrTiO}_3$  lattice consequent on hydrogen firing follows essentially the same mechanism as that for the formation of colloids in alkali halides and silver halides. It may not be out of place to mention here that we have observed the formation of similar iron colloid clusters in hydrogen-fired Fe-doped  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{SnO}_2$ . Indeed, Wertheim<sup>20</sup> has mentioned that when an Fe-doped  $\text{Al}_2\text{O}_3$  lattice was reduced, he obtained the Zeeman-split spectrum indicating the formation of iron colloids.

In addition to the Zeeman-split spectrum we observed an additional line whose intensity increases at the cost of the intensity of the Zeeman-split spectrum as iron concentration is reduced. It is tempting to think that this single line may be due to the presence of unrelaxed superparamagnetic small particles of iron whose spin relaxation time  $\tau$  is less than  $\hbar/h\nu \approx 10^{-9}$  sec for a hf field of 330 kOe.<sup>21</sup> The isomer shift of this single

<sup>14</sup> J. H. Schulman and W. D. Compton, *Color Centers* (Pergamon Press, Inc., New York, 1962), Chap. IX.

<sup>15</sup> J. H. Schulman, R. J. Ginther, and C. C. Klick, *J. Opt. Soc. Am.* **40**, 854 (1950).

<sup>16</sup> R. F. Tucker, Jr., *Phys. Rev.* **112**, 725 (1958).

<sup>17</sup> W. D. Compton, *Phys. Rev.* **107**, 1271 (1957).

<sup>18</sup> H. W. Etzel and D. A. Patterson, *Phys. Rev.* **112**, 1112 (1958).

<sup>19</sup> R. W. Davidge, *J. Mater. Sci.* **2**, 339 (1967).

<sup>20</sup> G. W. Wertheim and H. J. Guggenheim, in *Application of the Mössbauer Effect in Chemistry and Solid State Physics* (International Atomic Energy Agency, Vienna, 1966), p. 225.

<sup>21</sup> H. H. Wickman, M. P. Klein, and D. A. Shirley, *Phys. Rev.* **152**, 345 (1966).

line is  $-0.30 \pm 0.04$  mm/sec, which is slightly different from the isomer shift of the split spectrum ( $-0.20 \pm 0.04$  mm/sec). It is interesting to point out that in the ME study of cobalt particles precipitated in copper by Nasu *et al.*,<sup>22</sup> and similarly in the ME study of Cu-Fe alloy system by Ron *et al.*,<sup>23</sup> they have observed a Zeeman-split spectrum and an additional line. In both cases the additional line has been explained as being due to paramagnetic iron in the lattice and/or unrelaxed superparamagnetic particles. We believe that the additional line in our system is due to unrelaxed superparamagnetic particles.

On refiring these samples in air at 1000°C for 3 h

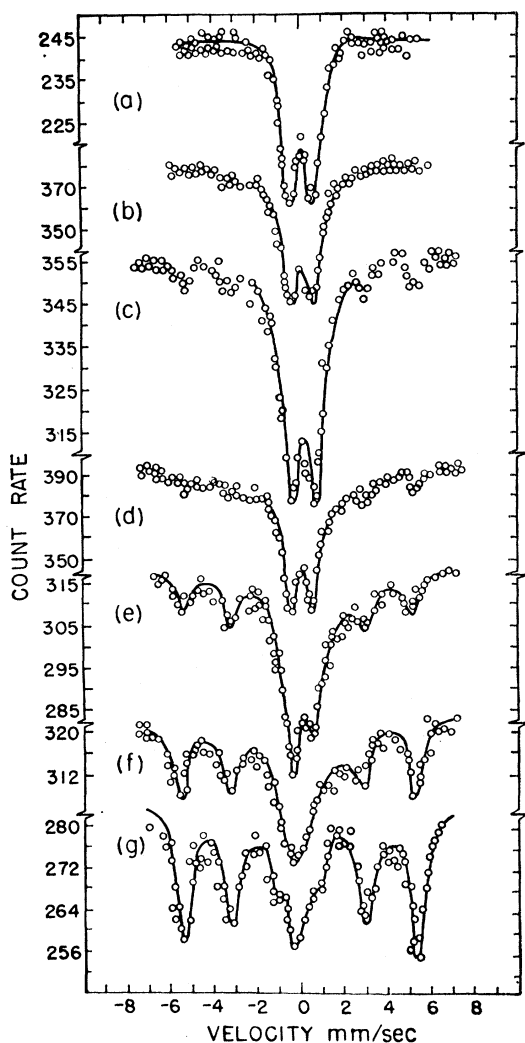


FIG. 3. Spectra obtained with 3-at.%-doped sample. (a) Air-fired sample; (b) sample fired in hydrogen at 400°C, (c) at 500°C, (d) at 600°C, (e) at 800°C, (f) at 900°C, and (g) at 1000°C, each time for 2 h.

<sup>22</sup> S. Nasu, T. Shinjo, Y. Nakamura, and Y. Murakami, *J. Phys. Soc. Japan* **23**, 664 (1967).

<sup>23</sup> M. Ron, A. Rosenzweig, H. Shechter, and A. Kidron, *Phys. Letters* **22**, 44 (1966).

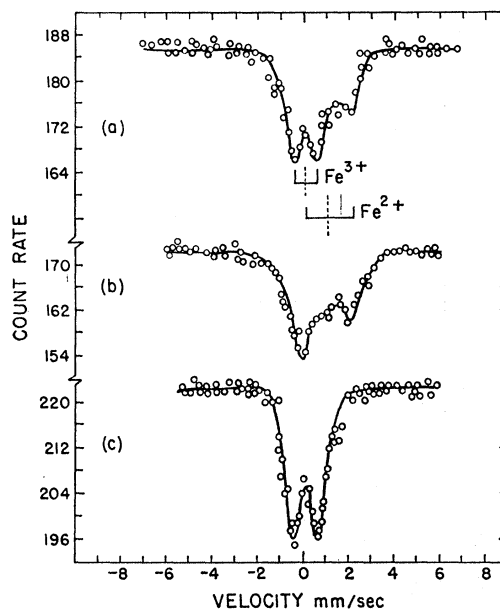


FIG. 4. Spectra obtained after successive vacuum firing at 1300°C for (a) 3 h and (b) 6 h. (c) Spectrum obtained after firing again in air at 1000°C.

we once again observe quadrupole-split spectra exactly like those shown in Fig. 1. This indicates that iron colloids are dispersed in the lattice to give once again Fe<sup>3+</sup> at Ti<sup>4+</sup> sites. We sought to examine the various stages through which the air-fired quadrupole-split spectrum transforms into the hydrogen-fired Zeeman-split spectrum. We started with a 3-at.% air-fired sample and annealed it in hydrogen at various temperatures ranging from 400 to 1000°C, each time for 2 h. When the sample was annealed at 500°C, the ME spectrum (at room temperature) showed an indication of the Zeeman-split spectrum emerging [Fig. 3(c)]. When the annealing was done at 600°C, the Zeeman-split spectrum became slightly stronger [Fig. 3(d)], whereas on annealing at 800°C and above we obtained a well-resolved Zeeman-split spectrum [Figs. 3(e) and 3(f)]. Indeed, it was found that the Zeeman-split spectrum rapidly emerges at and above 900°C. This is significant because it is at this temperature and above SrTiO<sub>3</sub> lattice begins to reduce.<sup>24,25</sup> Thus, it appears that the formation of the Zeeman-split spectrum is also associated with the reduction of the lattice.

We tried an alternate method to reduce the air-fired samples by heating them to high temperatures in vacuum. Figures 4(a) and 4(b) are the spectra for samples vacuum-annealed at 1300°C for 3 and 6 h, respectively. These spectra are substantially different from the spectra of Fig. 3, obtained after annealing in hydrogen. On analyzing the spectra, they are seen

<sup>24</sup> H. W. Gandy, *Phys. Rev.* **113**, 795 (1959).

<sup>25</sup> H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, *Phys. Rev.* **134**, A442 (1964).

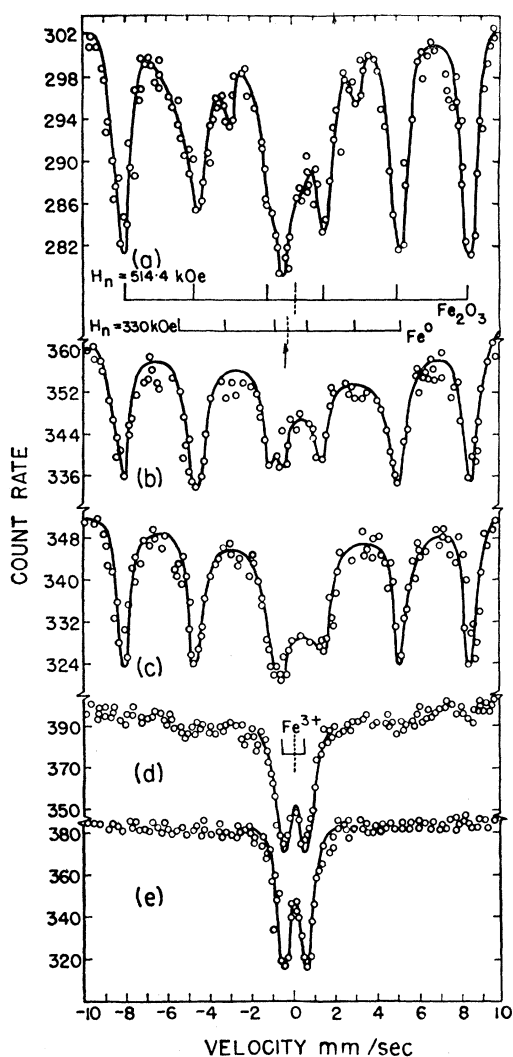


FIG. 5. Series of spectra obtained after successive air firing of hydrogen-annealed 3-at.-%-doped sample at (a) 500°C, (b) 600°C, (c) 800°C, (d) 900°C, and (e) 1000°C, for 2 h each time.

to be made up of two sets of quadrupole-split spectra, one attributable to the  $\text{Fe}^{3+}$  state and the other to the  $\text{Fe}^{2+}$  state, with quadrupole interactions  $\Delta E = 1.00$  and  $2.10$  mm/sec, and isomer shifts of  $0.10 \pm 0.04$  and  $1.10 \pm 0.04$  mm/sec, respectively. The quadrupole interaction for the  $\text{Fe}^{3+}$  state is the same as before. The quadrupole interaction observed for the  $\text{Fe}^{2+}$  state in the present series agrees very closely with that reported by us earlier in the  $\text{SrTiO}_3:\text{Co}^{37}$  system.<sup>4</sup> It appears, therefore, that in vacuum firing some of the  $\text{Fe}^{3+}$  ions are changed to  $\text{Fe}^{2+}$ . This is easy to understand because vacuum firing will reduce the lattice, and to compensate the charge, part of the  $\text{Fe}^{3+}$  ions will be converted to  $\text{Fe}^{2+}$  ions. Progressive vacuum firing increased the intensity of the  $\text{Fe}^{2+}$  state at the cost of the  $\text{Fe}^{3+}$  state, because of the enhanced reduction. Similar behavior

with respect to the change in the valence state of Fe and Cr ions in a MgO lattice has been reported by Hansler and Segelken,<sup>26</sup> and by Soshea *et al.*<sup>27</sup> It is indeed striking that if this vacuum-annealed sample is fired again in air at 1000°C for 3 h, we once again obtain the same quadrupolar spectrum. This shows that firing in air oxidizes the  $\text{Fe}^{2+}$  state to the  $\text{Fe}^{3+}$  state [Fig. 4(c)]. It is indeed interesting to note here that mere reduction of the lattice by vacuum firing does not give rise to metal colloids, but results only in the change of the valence state from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . It seems, therefore, that hydrogen firing is essential to the formation of metal colloids.

In another series of experiments we attempted to bring out the various stages through which the Zeeman-split spectrum for a hydrogen-annealed sample transforms into the air-fired quadrupole-split spectrum. The hydrogen-annealed sample was heated in air at various temperatures between 400 and 1000°C, each time for 2 h. The spectrum obtained after firing in air at 500°C was complex, and could be resolved into two sets of Zeeman-split spectra and a single line [Fig. 5(a)]. The hf fields for the two sets are roughly 514 and 330 kOe, and the isomer shifts are  $+0.1 \pm 0.04$  and  $-0.2 \pm 0.04$  mm/sec, respectively. The single line is at the same position, viz., at  $-0.30 \pm 0.04$  mm/sec. The two sets of Zeeman-split spectra are attributable to  $\text{Fe}_2\text{O}_3$  and Fe metal, respectively. The spectrum obtained after annealing the sample in air at 600°C is similar to that shown in Fig. 5(a), except that the lower-hf-field spectrum is considerably reduced in intensity, with a corresponding enhancement of the higher-hf-field spectrum. The single line is also considerably reduced in intensity [Fig. 5(b)]. On firing at 800°C the lower-hf-field spectrum has practically vanished. This series of experiments shows that on firing the sample in air, colloids of iron that are formed as a consequence of hydrogen annealing are converted into colloids of  $\text{Fe}_2\text{O}_3$ . Surprisingly enough, on further annealing of the samples in air at 900°C we get the familiar quadrupole-split spectrum with  $\Delta E = 1.0$  mm/sec and wings that indicate the existence of traces of  $\text{Fe}_2\text{O}_3$ . Annealing of the sample at 1000°C removes the wings. This shows that the colloids of  $\text{Fe}_2\text{O}_3$  that were formed reacted with the lattice above 800°C to give  $\text{Fe}^{3+}$  at  $\text{Ti}^{4+}$  sites.

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<sup>26</sup> R. L. Hansler and W. G. Segelken, *J. Phys. Chem. Solids* **13**, 124 (1960).

<sup>27</sup> R. W. Soshea, A. J. Dekker, and J. P. Sturtz, *J. Phys. Chem. Solids* **5**, 23 (1958).