$(NCS)_2$. The value of this frequency, assigned to ν_s (NCS), clearly indicates a Zn–NCS structure. The same spectral inspection for the cobalt(II) complexes $Co[P(C_6H_{11})_3]_2X_2$ and $Co[OP(C_6H_{11})_3]_2X_2$ does not permit one to locate absorption bands characteristic of coordinated NCS groups in the 690–900 cm.$^{-1}$ region. This can be easily understood since the spectrum of $Zn[P(C_2H_5)_3]_2(NCS)_2$ shows that the intensity of the CS band is very low.

Thus the low intensity of the CS stretching absorption and the probable overlap with the absorption bands of the partner ligands $[P(C_6H_{11})_3$ and $OP(C_6H_{11})_3]$ does not permit the localization of the CS band in the cobalt complexes under discussion. With the tetrahedral complexes $ML_2(NCS)_2$[32] one is faced with the same difficulty already encountered with the *cis* square-planar complexes of the same symmetry.

The low intensity of the CS band may have been the origin of a wrong interpretation of the spectrum of $Co[P(C_6H_5)_3]_2(CNS)_2$. Assignment of a band at 760 cm.$^{-1}$ to the CS stretching has led to the attribution of a thiocyanate structure to this compound.[22] However, comparison of the spectra of $Co[P(C_6H_5)_3]_2Cl_2$ and $Co[P(C_6H_5)_3]_2Br_2$ with the spectrum of $Co[P(C_6H_5)_3]_2(NCS)_2$ shows that the presence of a low-intensity CS stretching band cannot be ruled out in the 830 cm.$^{-1}$ region. Both in the 760 and 830 cm.$^{-1}$ regions absorption bands typical of the $P(C_6H_5)_3$ ligand are present, and therefore the assignment of a low-intensity band in these regions is very difficult.

Again, intensity measurements in solution in the CN stretching region can offer the basis for a better diagnostic criterion on the type of coordination. In this region one observes a doublet at 2085, 2064 cm.$^{-1}$ for the solid $Zn[P(C_2H_5)_3]_2(NCS)_2$. This splitting is presumably due to the in-phase and out-of-phase asymmetric stretching vibration of the two NCS groups tetrahedrally coordinated to zinc. A similar doublet is observed for the cobalt(II) complexes discussed here. The absorption bands in the 2100 cm.$^{-1}$ region of the zinc and cobalt complexes in $ClCH_2–CH_2Cl$ solution are strongly asymmetric on the side of the high frequencies. This can be explained as due to a doublet structure as found for the solid samples. The value of $\epsilon_{max} \times \Delta\nu_{1/2}$ for all of these complexes (Table IV) is in the range found for M–NCS coordination (Table II).

The results presented here are believed to be a useful basis for a further wide application to studies in solution on the coordination of triatomic groups to metal ions.

Acknowledgments.—The author wishes to express his appreciation to Professor A. Turco for the revision of the manuscript and for helpful discussions. The technical assistance of Miss Franca Marzola is gratefully acknowledged.

[32] Detailed structural discussion is not the aim of the present work. To suggest an explanation of the CN stretch splitting a C_{2v} symmetry is assumed for these tetrahedral complexes.

Contribution from the Bell Telephone Laboratories, Inc.,
Murray Hill, New Jersey

A Study of the Thermal Decomposition of Some Complex Oxalates of Iron(III) Using the Mössbauer Effect[1]

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Received September 30, 1965

Mössbauer spectra were measured at room temperature for the compounds $Fe_2(C_2O_4)_3 \cdot 6H_2O$, $Ba_3[Fe(C_2O_4)_3]_2 \cdot 8H_2O$, and $Sr_3[Fe(C_2O_4)_3]_2 \cdot 2H_2O$. Values of the isomer shift relative to $Cu(Co^{57})$ are +0.15, +0.03, and +0.16 mm./sec. and the quadrupole splittings are 0.57, 0.32, and 0.44 mm./sec., respectively. The alkaline earth compounds were heated to 1000°, and the iron(III) oxalate was heated to 600° in air at an approximate rate of 200°/hr. Samples were extracted at various temperatures and quenched, and their Mössbauer spectra were measured. The changing oxidation state of iron is clearly followed through the course of the decompositions. For example, the oxidation state of iron in the strontium compound is converted completely to +2 at 300° and reverts to +3 by 400°. At 700° a significant percentage is present as +4 which is gradually reduced to +3 with increasing temperature. The nature of these decompositions is discussed, and the results of the Mössbauer measurements are correlated with previous work on the thermal analysis of these materials. The iron(III) oxide formed in the early stages of the decomposition exhibits superparamagnetism.

Introduction

Recent investigation of the thermal decomposition of barium and strontium trisoxalatoferrates(III) and iron(III) oxalate suggests that frequent changes in the oxidation state of the iron atom occur during the decomposition.[2] Thermal analysis techniques yield only indirect evidence of such changes. The Mössbauer effect, however, can be used to obtain a more direct indication of the valence state of the iron atom. Mössbauer parameters have been well established for the

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[1] Presented in part at the Symposium on Mössbauer Effect, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 5, 1965.

[2] P. K. Gallagher, *Inorg. Chem.*, **4**, 965 (1965).

TABLE I

SUMMARY OF THE MÖSSBAUER PARAMETERS FOR IRON(III) OXALATE AND BARIUM AND STRONTIUM TRISOXALATOFERRATES(III) AT VARIOUS POINTS DURING THEIR THERMAL DECOMPOSITION[a]

Temp of calcination, °C.	Temp of measurement, °K.	Primary			Secondary		
		IS	Quad	Mag	IS	Quad	Mag
$Fe_2(C_2O_4)_3 \cdot 6H_2O$							
25	300	+0.15	0.57	0	...	...	...
25	4	+0.22	0.65	0	...	...	...
200	300	+0.93	2.27	0	+0.15	0.70	0
300	300	+0.067	...	487	+0.09	0.92	0
300	78	+0.18	...	512	...	...	...
300	4	+0.17	...	518	...	...	...
400	300	+0.067	...	490	...	...	...
500	300	+0.067	...	489	...	...	...
$Sr_3[Fe(C_2O_4)_3]_2 \cdot 2H_2O$							
25	300	+0.16	0.44	0	...	...	...
25	78	+0.23	...	0	...	...	...
25	4	+0.23	...	0	...	...	...
200	300	+0.95	2.3	0	+0.17	0.52	0
300	300	+0.97	2.2	0	...	...	...
400	300	+0.11	0.70	0	...	...	...
400	4	+0.17	...	503	...	...	...
500	300	+0.04	0.71	0	...	...	...
600	300	−0.05	0.74	0	...	...	..
700	300	−0.22	0	0	+0.33[c]	...	0
1000	300	−0.26	0	0	+0.26[c]	...	0
1200	300	−0.26	0	0	+0.30[c]	...	0
1000[b]	300	−0.27	0	0	+0.20[c]	...	0
1000[b]	4	−0.2[d]	...	~228	+0.1[d]	...	~435
$Ba_3[Fe(C_2O_4)_3]_2 \cdot 8H_2O$							
25	300	+0.03	0.32	0	...	...	...
25	4	+0.24	...	0	...	...	...
200	300	+0.97	2.14	0	...	...	...
300	300	+0.95	2.2	0	+0.15	...	0
400	300	+0.13	...	0	...	...	...
400	4	+0.02	...	505	~0.0	Broad	0
600	300	~0.0	...	~470	~0.0	Broad	0
800	300	−0.5	...	472	~0.0	...	0
1000	300	0.00	...	472	+0.13	...	0
700[b]	300	−0.22	0	0	+0.40[c]	...	0
1000[b]	300	−0.38	0	0	+0.20[c]	...	0
1000[b]	4	−0.1[d]	...	~230	+0.3[d]	...	~445

[a] Isomer shift (IS) is relative to a copper source and is in units of millimeters per second. The units of quadrupole (quad) and magnetic (mag) hyperfine splitting are millimeters per second and koersteds, respectively. [b] These samples have been slow-cooled, in contrast to the others which have been quenched. [c] These values may represent only a portion of a quadrupole split transition, half of which is concealed by the spectrum of another component. [d] The values for these samples are based on just the outer lines of the magnetic hyperfine splitting and are only approximate.

common oxidation states of iron,[3] and some measurements have been made of iron(IV).[4–6] This unusual oxidation state has been postulated as an intermediate during the decomposition of the barium[2,7] and strontium[2] trisoxalatoferrates(III). The purpose of this work, therefore, is to utilize the Mössbauer effect to substantiate the changes in oxidation state proposed from the thermal analysis investigation.

Experimental Procedures and Results

Reagent grade iron(III) oxalate was used, and the barium and strontium trisoxalatoferrates(III) were prepared as previously described.[2] Samples of each compound were heated in platinum crucibles at the rate of 200°/hr. in air. Crucibles were removed at 100° intervals beginning at 200° and cooled rapidly by plunging them into water. The samples were examined by X-ray diffraction using a GE-XRD-3 diffractometer. Selected samples were heated in air for 2 days at 700 or 1000° in order to more nearly approach equilibrium. These samples were cooled slowly in air to allow for the pickup of additional oxygen.[8,9]

The Mössbauer apparatus employed has been described elsewhere.[10] The source was Co^{57} diffused into copper. The shift of metallic iron relative to this source is −0.24 mm./sec. The sample thickness, 3 ± 2 mils, was adjusted so that the counting rate was approximately $1/e$ that of the rate without the sample. This frequently led to very low values of absorption thickness, in terms of milligrams of iron per square centimeter, particularly

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[3] G. K. Wertheim, "Mössbauer Effect, Principles and Application," Academic Press Inc., New York, N. Y., 1964, Chapter V.

[4] G. Shirane, D. E. Cox, and S. L. Ruby, *Phys. Rev.*, **125**, 1158 (1962).

[5] P. K. Gallagher, J. B. MacChesney, and D. N. E. Buchanan, *J. Chem. Phys.*, **41**, 2429 (1964).

[6] P. K. Gallagher, J. B. MacChesney, and D. N. E. Buchanan, *ibid.*, **43**, 516 (1965).

[7] S. W. Derbyshire, A. C. Fraker, and H. H. Stadelmaier, *Acta Cryst.*, **14**, 1293 (1961).

[8] J. B. MacChesney, R. C. Sherwood, J. F. Potter, and H. J. Williams, *J. Chem. Phys.*, **43**, 1907 (1965).

[9] J. B. MacChesney, J. F. Potter, R. C. Sherwood, and H. J. Williams, *ibid.*, **43**, 3317 (1965).

[10] C. R. Kurkjian and D. N. E. Buchanan, *Phys. Chem. Glasses*, **5**, 63 (1964).

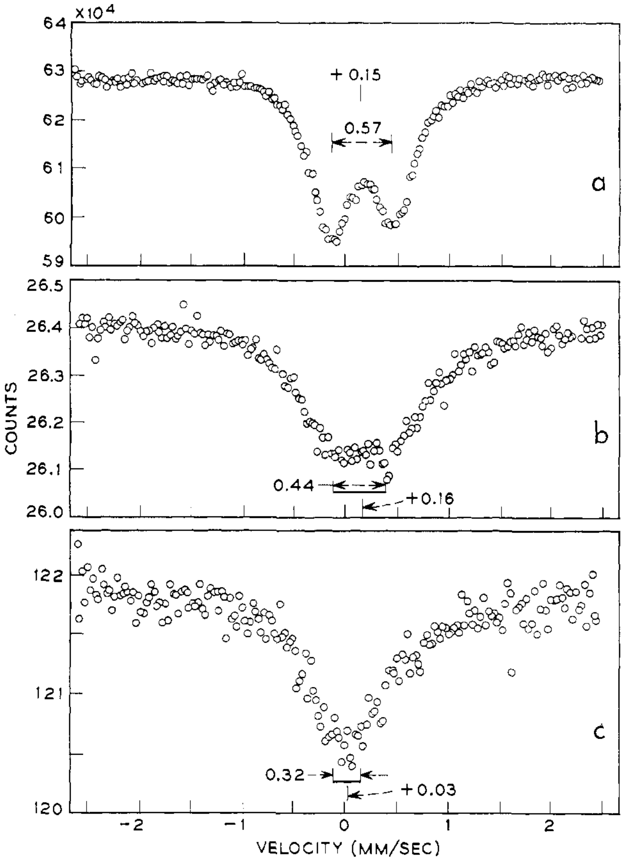

Figure 1.—Mössbauer spectra, at 300°K., of some complex oxalates of iron(III): (a) iron(III) oxalate, uncalcined; (b) strontium trisoxalatoferrate(III), uncalcined; (c) barium trisoxalatoferrate(III), uncalcined.

in the case of the complex oxalates. Most measurements were made at room temperature, and the centroids were used to calculate the isomer shifts of spectra exhibiting magnetic hyperfine splitting. In several cases spectra were measured at low temperatures in an effort to characterize the samples better and differentiate between the components.

Results

The results of the Mössbauer measurements are summarized in Table I. Figures 1–6 present pertinent spectra associated with the decomposition of the iron(III) oxalate and the alkaline earth trisoxalatoferrates(III).

Discussion

The Mössbauer spectra of the three compounds at room temperature prior to calcination are displayed in Figure 1. The iron(III) oxalate and strontium trisoxalatoferrate(III) have very similar patterns, as would be expected. The barium salt, however, has a less positive isomer shift and reduced quadrupole splitting. All are within the characteristic region associated with trivalent iron. Brady, *et al.*,[11,12] report an isomer shift of 0.14 mm./sec. (corrected to a Cu source) and a quadrupole splitting of 0.5 mm./sec. for an unspecified hydrate of iron(III) oxalate at room temperature. This is in excellent agreement considering the amorphous nature of the compound. They similarly report 0.04 and 1.0 mm./sec. for the corresponding values of ammonium trisoxalatoferrate(III). This isomer shift is virtually identical with the result for the barium salt. The quadrupole splitting indicates increasing distortion around the iron in the series of trisoxalatoferrates(III) $NH_4 > Sr > Ba$. Although the barium and ammonium ions are essentially the same size, they are different in charge and number. Therefore, the difference in quadrupole splitting is not unexpected.

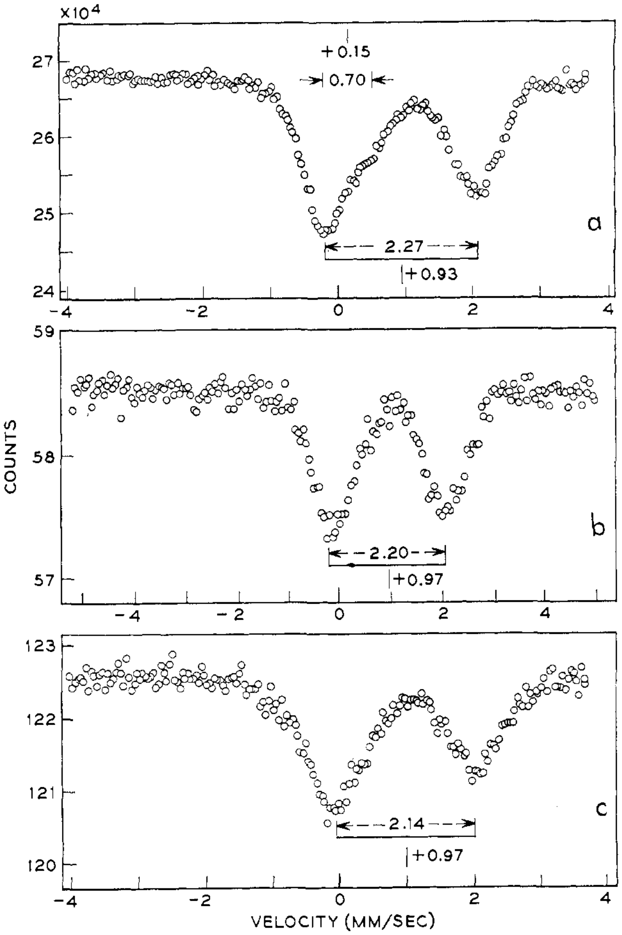

Figure 2.—Mössbauer spectra, at 300°K., exhibiting the formation of iron(II) during the thermal decomposition of some complex oxalates: (a) iron(III) oxalate, calcined at 200°; (b) strontium trisoxalatoferrate(III), calcined at 300°; (c) barium trisoxalatoferrate(III), calcined at 200°.

The Mössbauer spectra of the three uncalcined salts at low temperature do not reveal any magnetic interactions for these materials. The isomer shifts as a function of temperature (see Table I) are in the direction expected from the second-order Doppler effect.

It was inferred from the thermal analysis data that the early stages of the decomposition involved the reduction of iron(III) to iron(II).[2] This is clearly proven by the spectra shown in Figure 2. All three compounds which have been heated to 200–300° have spectra with large positive isomer shifts and quadrupole splittings as indications of divalent iron. The more negative peak is considerably larger in all instances, and

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(11) P. R. Brady, P. R. Wigley, and J. F. Duncan, *Rev. Pure Appl. Chem.*, **12**, 165 (1962).

(12) P. R. Brady and J. F. Duncan, *J. Chem. Soc.*, 653 (1964).

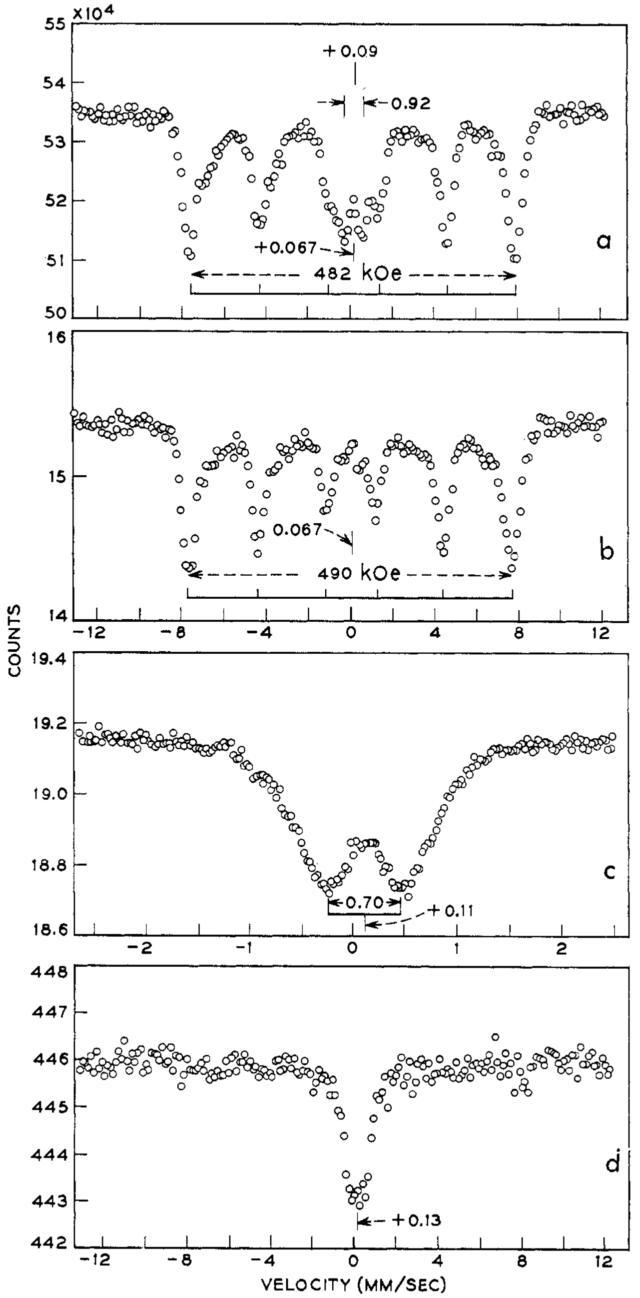

Figure 3.—Mössbauer spectra, at 300°K., exhibiting the formation of superparamagnetic iron(III) oxide during the thermal decomposition of some complex iron(III) oxalates: (a) iron(III) oxalate, calcined at 300°; (b) iron(III) oxalate, calcined at 400°; (c) strontium trisoxalatoferrate(III), calcined at 400°; (d) barium trisoxalatoferrate(III), calcined at 400°.

a trivalent component is evident in Figure 2a. Similar trivalent components may be present in the other spectra as well. Theory, however, does not require that each branch of the doublet be of equal size,[13] and consequently it is not necessary to invoke the presence of iron(III) to explain Figures 2b and c.

The Mössbauer pattern of iron(II) oxalate dihydrate has been extensively investigated.[12,14] Unfortunately there is no plateau corresponding to the anhydrous salt in the thermal analysis curve of this material.[15,16] Consequently, the anhydrous salt is not readily prepared by simple drying procedures, and its Mössbauer spectrum has not been previously determined. The values associated with the dihydrate at room temperature are 1.02 and 1.7 mm./sec. for the isomer shift and quadrupole splitting, respectively.[12] The isomer shift value from the compilation by Fluck, *et al.*,[17] also for the dihydrate, is 0.98 mm./sec., which is closer to the value observed for the anhydrous material in this paper. In either case there can be no doubt that iron(III) is reduced to iron(II) at an early step in the thermal decomposition of the trisoxalatoferrate(III) ion.

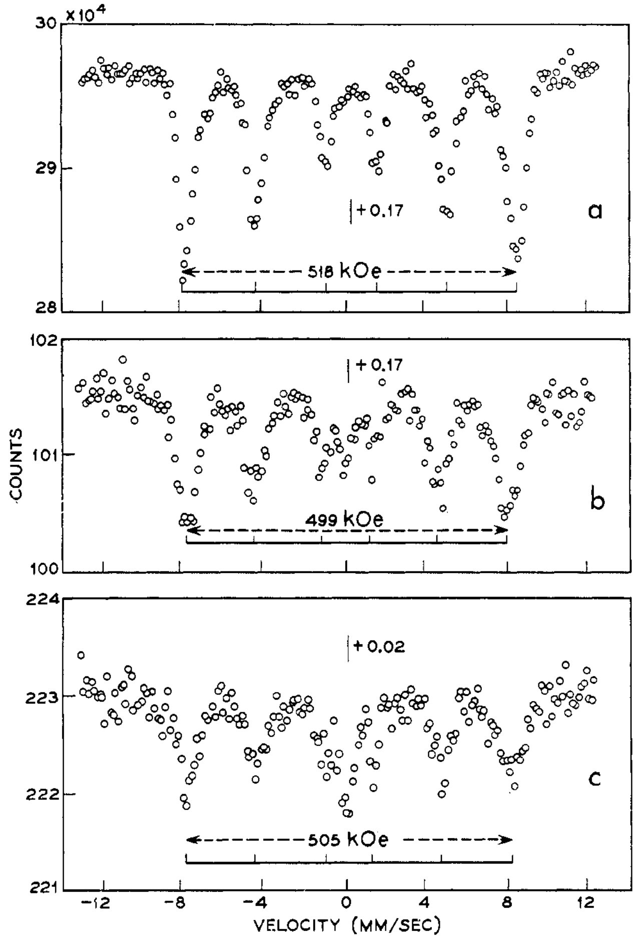

Figure 4.—Mössbauer spectra, at 4°K., showing less superparamagnetic material: (a) iron(III) oxalate, calcined at 300°; (b) strontium trisoxalatoferrate(III), calcined at 400°; (c) barium trisoxalatoferrate(III), calcined at 400°.

Figure 3 reveals that the iron has been reoxidized to iron(III) in the region of 300–400°, as predicted from the thermal analysis of these compounds. The weight loss data are such that these materials have been converted to iron(III) oxide or mixtures of this oxide and the appropriate alkaline earth carbonate.[2] X-Ray diffraction patterns of these materials reveal no line structure, suggesting that they are amorphous or have a very small particle size. Bulk iron(III) oxide is

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(13) V. I. Goldanskii, E. F. Makarov, and V. V. Khrapov, *Phys. Letters*, **3**, 344 (1963).

(14) F. D. S. Barros, P. Zorry, and L. E. Campbell, *ibid.*, **7**, 135 (1963).

(15) J. Robin, *Bull. Soc. Chim. France*, 1978 (1953).

(16) P. K. Gallagher and F. Schrey, *J. Am. Ceram. Soc.*, **47**, 434 (1964).

(17) E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem.*, **2**, 277 (1963).

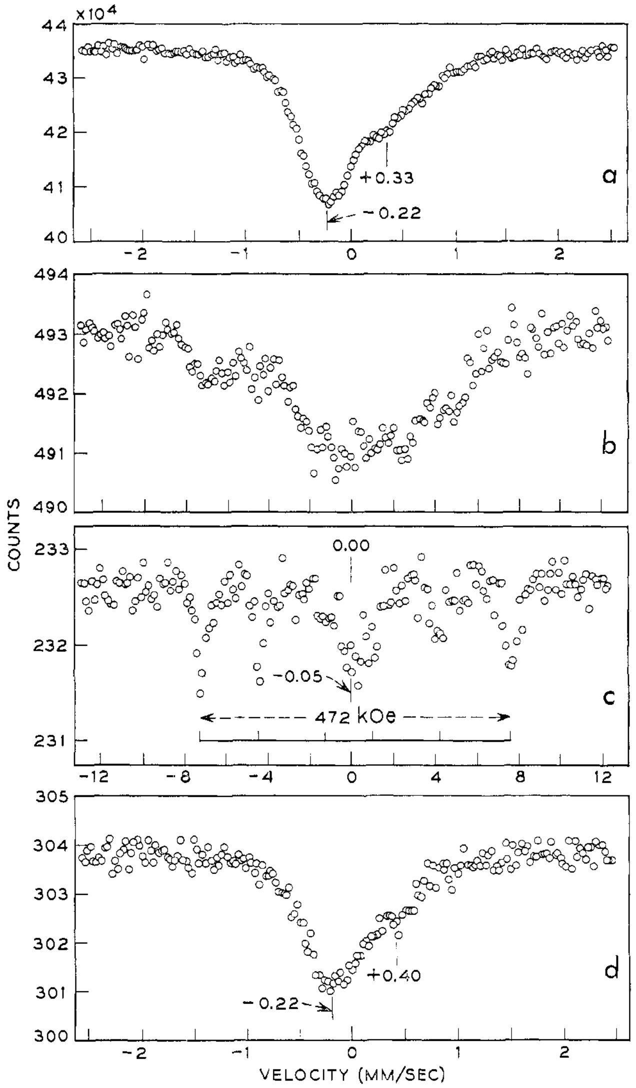

Figure 5.—Mössbauer spectra, at 300°K., indicating the formation of iron(IV) in the thermal decomposition of some complex oxalates of iron(III): (a) strontium trisoxalatoferrate(III), calcined at 700°; (b) barium trisoxalatoferrate(III), calcined at 600°; (c) barium trisoxalatoferrate(III), calcined at 800°; (d) barium trisoxalatoferrate(III), calcined at 700° and cooled slowly.

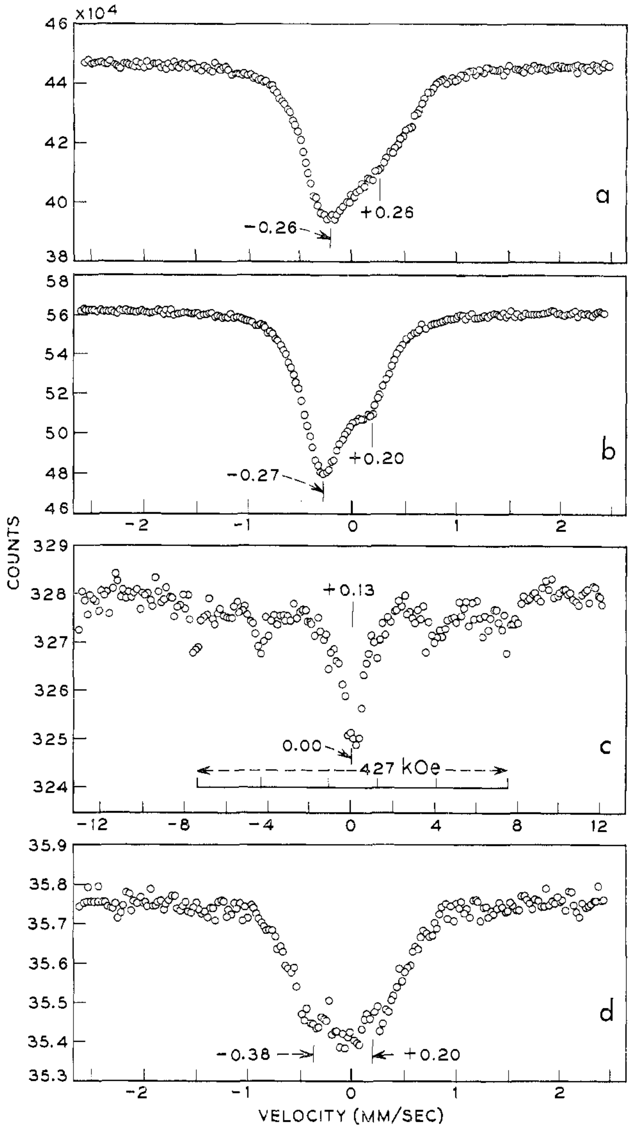

Figure 6.—Mössbauer spectra, at 300°K., of complex oxalates of iron(III) which have been calcined at 1000°: (a) strontium trisoxalatoferrate(III), calcined at 1000°; (b) strontium trisoxalatoferrate(III), calcined at 1000° and cooled slowly; (c) barium trisoxalatoferrate(III), calcined at 1000°; (d) barium trisoxalatoferrate(III), calcined at 1000° and cooled slowly.

antiferromagnetic with a Neel temperature around 700°.[18] The spectrum of iron(III) oxalate which had been calcined at 400°, presented in Figure 3, is the typical six-line pattern associated with magnetically oriented iron(III). The magnetic hyperfine splitting is significantly less than the normal value for iron(III) oxide of 515 koersteds.[19] The similar material calcined at 300° (Figure 3a) shows a paramagnetic trivalent component, and the spectra of the alkaline earth trisoxalatoferrate(III) exhibit only a trivalent paramagnetic spectrum. Nakamura, *et al.*,[20,21] have examined the Mössbauer spectra of finely divided iron(III) oxide, prepared by the thermal decomposition of α-iron(III) oxide hydrate, and have observed a similar paramagnetic component which they attribute to "superparamagnetism."[22] In this condition the anisotropy energy, which is proportional to the volume of the particle, is reduced to a value comparable to the thermal energy kT, and, hence, the magnetic alignment is destroyed by thermal motion. Superparamagnetism has also been observed in certain fine-grained ferrites.[23]

Measuring the Mössbauer effect at sufficiently lower temperatures should restore the magnetic hyperfine splitting. Figure 4 shows the spectra of the appropriate samples at 4°K. The spectrum (Figure 4a) of iron(III) oxalate calcined at 300° no longer has a paramagnetic component, and the hyperfine splitting has increased to the more normal value. Table I indicates that this was also true at 78°K. The spectrum of the

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(18) P. Gilad, M. Greenshpan, P. Hillman, and H. Schechter, *Phys. Letters*, **7**, 239 (1963).

(19) O. C. Kistner and A. W. Sunyar, *Phys. Rev. Letters*, **4**, 412 (1960).

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(21) T. Nakamura, T. Shinjo, Y. Endoh, N. Yamamoto, M. Shiga, and Y. Nakamura, *Phys. Letters*, **12**, 178 (1964).

(22) C. P. Bean, *J. Appl. Phys.*, **26**, 1381 (1955).

(23) W. J. Schuele, S. Shtrikman, and D. Treves, *ibid.*, **36**, 1010 (1965).

alkaline earth carbonate and iron(III) oxide mixture (Figures 4b and c) indicates some superparamagnetic material remains at 4°K., but the major portion has been converted to the antiferromagnetic form. The slightly lower values of the magnetic hyperfine splitting for these samples (Table I) are consistent with the incomplete or reduced magnetic ordering.

The hematite formed by the decomposition of the iron(III) oxalate does not undergo further chemical change in the temperature region investigated. The mixture of the alkaline earth carbonate and finely divided iron(III) oxide, however, reacts, sequentially, to form two series of interesting compounds, $MFeO_{3-x}$ and $M_3Fe_2O_{7-x}$, in which a significant fraction of the iron is present as iron(IV). The Mössbauer effect in the first series has already been investigated[5,6] and similar studies are in progress on the latter series.

Figure 5 presents Mössbauer spectra of samples in the temperature region, indicated by thermal analysis,[2] in which the iron(IV) species are initially formed. The spectrum of the strontium compound exhibits a large peak having an isomer shift associated with iron(IV)[5] and is thus in complete agreement with the predictions of the thermal analysis. A smaller peak is evident which corresponds to the trivalent component. Figures 5b and c, for the analogous quenched samples of the barium salt, do not have any portions which can be attributed to iron(IV), but rather show only the spectra of iron(III) with the increasing magnetic hyperfine splitting at higher temperatures predicted from the crystallite growth and concomitant destruction of superparamagnetism. If, however, the same samples are allowed to cool slowly in air from these temperatures, a spectrum such as shown in Figure 5d is obtained. In this latter case the spectrum resembles that of the strontium compound, and iron(IV) and iron(III) portions can be readily distinguished.

There are two possible explanations for the difference in behavior of the strontium and barium materials depending upon the efficiency of the quenching operation. If it is assumed that the quench was effective, then it must be concluded that the actual decomposition processes of the barium and strontium salts are different in spite of their other similarities.[2] Alternatively, the kinetics of oxygen uptake may be very different for the two compounds, and as a result the rapid cooling is ineffective in preventing an uptake of oxygen and the concomitant oxidation of the iron in the strontium material.

Above approximately 800° the remaining alkaline earth carbonate decomposes and simultaneously reacts with the alkaline earth ferrate to form a composition in the system $M_3Fe_2O_{7-x}$.[2] Figures 6a and c are spectra of the rapidly cooled materials while Figures 6b and d are of the slow-cooled samples. The interpretation of the spectra is similar to that of the previous samples at 700–800°. Comparison of the slow-cooled barium samples at 700 and 1000° (Figures 5d and 6d) indicates an apparently higher concentration of iron(IV) in the material cooled from the lower temperature. There are many factors which may account for this, *e.g.*, kinetic factors due to the incorporation of another atom of barium or increased perfection and growth of the particle which affect the uptake of oxygen on actual reduction in the stable iron(IV) content in the $M_3Fe_2O_{7-x}$ system, or the possible contributions of the trivalent spectrum to that assigned to iron(IV). The latter factor arises from the possible quadrupole splitting of the trivalent spectrum such that the less positive portion is superimposed upon the spectrum of iron(IV).[5,6]

The spectra, at 4°K., of the samples which were cooled slowly from 1000° indicate that there are not sufficient oxygen vacancies present to disrupt the magnetic ordering within these systems. The resolution is not good. However, the outer lines of the trivalent and quadrivalent components can be readily distinguished, and the interpretation is similar to that previously noted.[4,5] The approximate values of the isomer shift and magnetic hyperfine splitting are presented in Table I.

Conclusions

During the thermal decomposition of iron(III) oxalate and barium and strontium trisoxalatoferrates(III), the oxidation state of the iron undergoes several changes. In all three compounds the iron is initially reduced to iron(II) at about 250°. The next step involves the formation of iron(III) oxide having a very small particle size and consequently exhibiting superparamagnetism. As the temperature is increased, the crystallites grow and supermagnetism disappears. In the alkaline earth trisoxalatoferrates(III) the products of the initial decomposition, iron(III) oxide and alkaline earth carbonate, react further at higher temperatures to form materials in the system $M_3Fe_2O_{6.0-7.0}$. The iron(IV) content of these materials is highly variable and dependent upon their subsequent treatment. The presence of the unusual oxidation state of iron(IV), however, is clearly demonstrated by the Mössbauer effect.

Acknowledgment.—The authors are grateful to Mr. E. A. Sigety for experimental assistance.