

# Hyperfine Structure of Divalent and Trivalent $\text{Fe}^{57}$ in Cobalt Oxide

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The hyperfine structure of divalent and trivalent iron in  $\text{CoO}$  has been obtained from the Mössbauer effect of  $\text{Fe}^{57}$  produced by the electron-capture decay of  $\text{Co}^{57}$ . The two valence states are obtained respectively by x ray and Auger effect de-excitation of the  $K$ -shell hole resulting from electron capture in divalent  $\text{Co}^{57}$ . Higher valence states which could be produced by multiple Auger de-excitation are not observed, indicating that their lifetimes are short. The magnetic field at a divalent iron nucleus at low temperature is  $2.0 \times 10^6$  oe while that at a trivalent one is  $5.6 \times 10^5$  oe. The quadrupole coupling in this almost cubic environment is less than 1.0 Mc/sec.

## INTRODUCTION

RECENT studies of magnetic fields at  $\text{Fe}^{57}$  nuclei using the Mössbauer effect<sup>1</sup> have shown that a field of  $5.0 \times 10^5$  to  $5.5 \times 10^5$  oe is characteristic of trivalent iron in a number of compounds.<sup>2</sup> The corresponding value for divalent iron appears to depend more strongly on the crystalline environment, but the available information is limited. Further experiments in substances like the divalent transition metal oxides, whose magnetic structure and properties are well known,<sup>3,4</sup> are of considerable interest. The additional fact that both the iron and the cobalt compound exist and have the same crystal structure makes them particularly attractive for  $\text{Fe}^{57}$  Mössbauer effect studies.

Cobalt oxide is an antiferromagnetic cubic material with a Néel temperature of  $291^\circ\text{K}$ . Above this temperature it is cubic and has the sodium chloride structure; below, it contracts along one of the cubic principal axes and becomes tetragonal. The distortion amounts to 1.2%. The direction of the magnetization has been found to lie about  $10^\circ$  from the  $c$  axis. The divalent iron oxide has the same crystal structure and a Néel temperature of  $198^\circ\text{K}$ . Below that temperature it elongates along a  $[111]$  direction, becoming rhombohedral. The direction of magnetization is perpendicular to a  $(111)$  plane.

An experiment of the type proposed above can advantageously be done by incorporating  $\text{Co}^{57}$  into  $\text{CoO}$ . Such an experiment may, however, give rise to some difficulty because of the after-effects of the electron-capture decay<sup>5</sup> of  $\text{Co}^{57}$ , which produce multiply ionized atoms and excited atomic states. These have already been invoked to explain the hfs of  $\text{Fe}^{57}$  produced by the decay of  $\text{Co}^{57}$  in  $\text{Al}_2\text{O}_3$ ,<sup>6</sup> and as is well known,

can have a serious effect on angular correlations in dielectric materials.<sup>7</sup> These effects can be more definitively studied in  $\text{CoO}$ , where cobalt is a normal constituent of definite valence and lattice position. Moreover, the iron atoms resulting from the decay of  $\text{Co}^{57}$  are produced in sites very similar to those occupied by iron in  $\text{FeO}$ . (The recoil accompanying the electron capture decay is insufficient to displace the atom from its lattice site.) Such an experiment should also make it possible to study various valence states in the same almost cubic environment.

A measure of the relative frequency with which divalent and trivalent iron atoms are produced may be obtained from the fluorescent yield, which for iron is known to be 35%. That is, in 35% of all decays the excited iron atom emits a  $K$  x ray; in the rest it emits a  $K$  Auger electron. It is not correct to assume, however, that divalent iron is produced in 35% of all decays. Stable divalent iron is formed only when the x ray completely de-excites the atom, i.e., when it is a  $KM$  x ray. A  $KL$  x ray would almost certainly be followed by an Auger process from the  $M$  shell, i.e., an  $LMM$  Auger process, resulting in a trivalent iron atom. Trivalent iron is also produced directly by a  $KMM$  Auger process. Other, higher valence states may be produced by multiple Auger processes.<sup>8</sup> In fact, Snell and Pleasonton<sup>9</sup> have shown that the Auger effect is possible not only between the atomic shells but also between the subshells, making it possible to produce very highly ionized charge states in *free* atoms. It is clear, however, that the electron affinity of these states is so great that they will not exist for an appreciable length of time in a solid, but it is difficult to estimate the lifetime of a state such as  $\text{Fe}^{4+}$  in a medium such as  $\text{CoO}$ .

The  $\text{Fe}^{57}$  Mössbauer experiments reported in the past, in which the radioactive species was incorporated into a metal, show the presence of only one atomic state, a result in accord with theoretical estimates

<sup>1</sup> R. L. Mössbauer, *Z. Physik* **151**, 124 (1958).

<sup>2</sup> See R. E. Watson and A. J. Freeman, *Phys. Rev.* (to be published) for a recent review.

<sup>3</sup> C. G. Shull, W. A. Strauser, and E. D. Wollan, *Phys. Rev.* **83**, 333 (1951).

<sup>4</sup> W. L. Roth, *Phys. Rev.* **110**, 1333 (1958).

<sup>5</sup> See the discussions by I. Bergström, in *Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1955), p. 624.

<sup>6</sup> G. K. Wertheim, *Bull. Am. Phys. Soc.* **6**, 8 (1961). The situation in that case is relatively complicated since cobalt may enter the lattice both interstitially and substitutionally. There is also the possibility that two valence states of cobalt may be present initially.

<sup>7</sup> See the discussion by H. Frauenfelder, in *Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1955), p. 591. Also, B. G. Pettersson, J. E. Thun, and T. R. Gerholm, *Nuclear Phys.* **24**, 223 (1961).

<sup>8</sup> Pertinent references may be found in reference 6.

<sup>9</sup> A. H. Snell and F. Pleasonton, *Phys. Rev.* **100**, 1396 (1955).

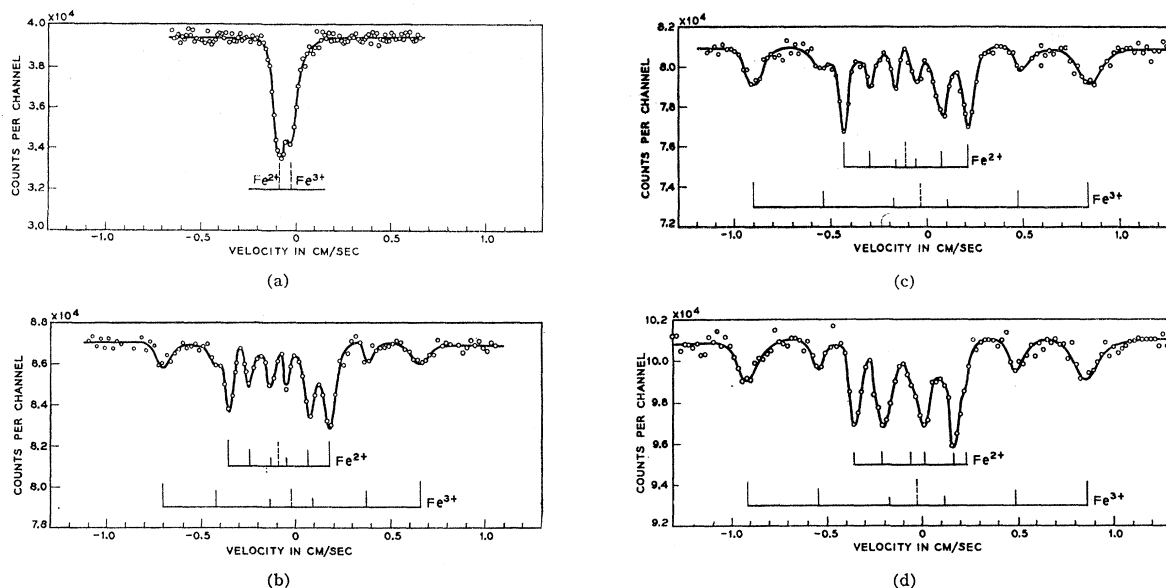


FIG. 1. Hyperfine structures of the 14.4-keV gamma transitions in divalent and trivalent  $\text{Fe}^{57}$  in cobalt oxide (a) at 298°K; (b) at 243°K; (c) at 169°K; (d) at 78°K.

which suggest that the relaxation time must be less than  $10^{-12}$  second. This time is short compared to the  $10^{-7}$ -second half-life of the first excited state of  $\text{Fe}^{57}$ , which here sets the time scale of observation. It is also in accord with the observation in the case of angular correlations that there is no disturbance attributable to this cause in metallic sources.

In the present experiments we expect to be able to distinguish much higher charge states. Their identification is greatly facilitated by the earlier studies of the (chemical) isomer shift<sup>10,11</sup> and of the magnetic fields at iron nuclei in various environments. The more detailed study of the isomer shift<sup>12</sup> also shows where previously unobserved higher valence states may be found.

#### EXPERIMENTAL

The sample was prepared from crystalline  $\text{CoO}$  which was powdered, coated with  $\text{Co}^{57}$  from an aqueous solution, dried, heated in a continuously pumped quartz tube to 1000°C for one hour, and then rapidly cooled. A 0.005-in. layer of the powder was then cemented to a copper sample holder which was placed in a vacuum Dewar. The absorber consisted of potassium ferrocyanide made with isotopically enriched  $\text{Fe}^{57}$ . The required Doppler velocity was provided by a dual voice-coil loudspeaker executing parabolic motion at a frequency of 3.5 cps. (Positive velocity corresponds to absorber moving toward source.) The desired 14.4-keV

gamma ray was selected with a conventional scintillation-counter spectrometer. A transistor modulator was used to combine the output of the single-channel pulse-height analyzer with that of the velocity sensing coil of the loudspeaker to produce pulses with amplitude proportional to the instantaneous velocity of the absorber. These pulses were then analyzed by a 256-channel analyzer which directly produces an absorption spectrum. Data were taken at four fixed points in temperature, 298°K, 243°K (liquid Freon), 169°K (liquid ethylene), and 78°K.

After completion of the Mössbauer measurements the sample was examined by x-ray diffraction.<sup>13</sup> The results indicated that the material had the structure of  $\text{CoO}$  and had not been oxidized in the diffusion process.

#### RESULTS AND DISCUSSION

The data obtained above the Néel temperature, Fig. 1(a), show two poorly resolved emission lines of unequal intensity. A two-line spectrum could arise from quadrupole splitting or from the presence of two nonequivalent types of iron, representing different lattice positions or different valence states. The interpretation based on quadrupole splitting may be ruled out immediately, since the intensities are unequal. (Electric field gradients may, however, be experienced by a substitutional impurity atom which is shifted from the lattice point of cubic symmetry.) The suggestion that the  $\text{Fe}^{57}$  atoms occupy other than normal Co lattice points is also not tenable, since before their decay these atoms are chemically indistinguishable from stable cobalt atoms, which were shown by x-ray

<sup>10</sup> O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters 4, 412 (1960).

<sup>11</sup> S. DeBenedetti, G. Lang, and R. Ingalls, Phys. Rev. Letters 6, 60 (1961).

<sup>12</sup> L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters 6, 98 (1961).

<sup>13</sup> The author is indebted to Mrs. V. B. Compton for the x-ray examinations.

TABLE I. Isomer shifts and magnetic fields at the nuclei of divalent and trivalent iron atoms in CoO. The isomer shift is measured with respect to a potassium ferrocyanide absorber. Its sign indicates that the energy of the gamma ray emitted by  $\text{Fe}^{57}$  in CoO is greater than the nuclear transition energy in the absorber. The magnetic fields may be assumed to be negative.<sup>2</sup>

Temp. (°K)	<i>H</i> at nucleus ( $10^5$ oe)		Isomer shift (cm/sec)	
	$\text{Fe}^{2+}$	$\text{Fe}^{3+}$	$\text{Fe}^{2+}$	$\text{Fe}^{3+}$
298	...	...	$0.087 \pm 4$	$0.023 \pm 4$
243	$1.69 \pm 3$	$4.26 \pm 5$	$0.093 \pm 4$	$0.025 \pm 4$
169	$2.00 \pm 3$	$5.44 \pm 6$	$0.118 \pm 4$	$0.036 \pm 4$
78	$1.8 \pm 1$	$5.57 \pm 6$	...	$0.034 \pm 4$

diffraction to form good CoO crystals. Moreover, it is extremely unlikely that the recoil associated with the neutrino of the electron capture process is sufficiently energetic to displace the atom from its lattice site. The data are consistent with an interpretation relating the two lines to two valence states of iron.

The data taken below the Néel temperature, Figs. 1(b) and (c), give further support to this interpretation. The lines shown in these figures have been grouped into two six-line hyperfine spectra. The lines belonging to each set were identified in part by their intensities, which are greater for the six lines grouped in the middle, and in part by their linewidths, which are smaller for these lines. The centroids of the resulting patterns in Fig. 1(b) coincide with the positions of the two lines observed above the Néel temperature, Fig. 1(a), confirming that the two lines correspond to two distinct types of iron. (The thermal red shift between 298° and 243°K, the two temperatures in question, is sufficiently small to be neglected here.)

The resulting six-line absorption patterns have the properties characteristic of pure magnetic hyperfine splitting of the 14.4-keV transition in  $\text{Fe}^{57}$ . The quadrupole coupling must be less than 1 Mc/sec. This is not surprising in view of the near-cubic symmetry of CoO, even in the antiferromagnetic state. A crude estimate based on a calculation of the field gradient due to the nearest neighbor oxygen ions indicates that the expected quadrupole coupling is at most only a small fraction of an experimental linewidth. As a result these experiments give no information concerning the direction of the magnetization, yielding only the magnetic field at the ion nuclei and the isomer shifts which are summarized in Table I.

The data show the presence of only two distinct types of iron which we have so far tentatively identified with two distinct charge states. It is clear, especially from an examination of Fig. 1(a), that other charge states cannot be present to an extent greater than 0.1 times the concentration of the two discussed so far. It is also reasonably clear that these two must represent the most stable divalent and trivalent charge states which are known to be produced by x ray and single Auger effect de-excitation, respectively. Further confirmation

comes from a comparison with the systematics of the isomer shift<sup>11</sup> which shows that the line with the smaller displacement from zero (0.023 cm/sec) corresponds in shift to those observed for trivalent iron compounds, while the line with the greater shift (0.087 cm/sec) corresponds to the less ionic divalent compounds such as FeS.

This identification is also consistent with the values given for the magnetic fields at the iron nuclei in Table I. A field of  $5.0 \times 10^5$  to  $5.5 \times 10^5$  oe has repeatedly been shown to be characteristic of compounds containing trivalent iron in octahedral coordination, e.g.,  $\text{Fe}_2\text{O}_3$ ,<sup>10</sup>  $\text{Fe}_3\text{O}_4$ ,<sup>14,15</sup> and yttrium iron garnet,<sup>16,17</sup> as well as for  $\text{Fe}^{3+}$  in  $\text{MgO}$ .<sup>18</sup> The value obtained here for the iron now identified as trivalent is  $5.6 \times 10^5$  oe at 0°K. In the case of divalent iron the situation is less clear-cut: a field of  $3.4 \times 10^5$  oe has been obtained for  $\text{FeF}_2$ ,<sup>14</sup> while a field of  $4.5 \times 10^5$  oe has been given for  $\text{Fe}^{2+}$  in  $\text{Fe}_3\text{O}_4$ .<sup>19</sup> The smaller field and greater variability in the case of divalent iron is not unexpected in view of possible large positive orbital contributions to the magnetic field. The value obtained here for  $\text{Fe}^{2+}$  is  $2.0 \times 10^5$  oe at 169°K where the field may be within 5% of its low-temperature limit. Further complications which arise at lower temperature are discussed below.

We return now to a discussion of the stability of the various charge states which are in principle produced by x-ray emission and by single as well as multiple Auger processes. A pertinent feature here is the linewidth, which was found to be greater for the trivalent than for the divalent iron. The divalent iron linewidth is not significantly different from that generally found. The larger linewidth of the trivalent iron can arise either because there are differences in the immediate environment of the trivalent atoms or because the trivalent charge state is unstable with a decay time not much different from  $10^{-7}$  sec. Differences in local environment can arise in the following way: Higher valence states such as  $\text{Fe}^{4+}$  (which are known to be formed but are not observed) decay by capturing an electron from a neighboring divalent Co atom, producing a trivalent iron atom with a nearest neighbor trivalent cobalt atom. In that way a wide range of local environments can be produced which will result in small differences in the field at the Fe nuclei. This process can in effect reduce all the higher charge states to trivalent iron on a time scale which must be short compared to  $10^{-7}$  sec.

The question of whether the trivalent iron is itself

<sup>14</sup> G. K. Wertheim, J. Appl. Phys. S. 32, 110 (1961).

<sup>15</sup> E. L. Boyd, L. J. Bruner, J. I. Budnick, and R. J. Blume, Bull. Am. Phys. Soc. 6, 159 (1961).

<sup>16</sup> C. Alf and G. K. Wertheim, Bull. Am. Phys. Soc. 5, 428 (1960).

<sup>17</sup> R. Bauminger, S. G. Cohen, A. Marinov, and S. Ofer, Phys. Rev. 122, 743 (1961).

<sup>18</sup> E. S. Rosenwasser and G. Feher, Bull. Am. Phys. Soc. 6, 117 (1961).

<sup>19</sup> R. Bauminger, S. G. Cohen, A. Marinov, S. Ofer, and E. Segal (to be published).

stable can be answered in part by referring to the relative intensities of the divalent and trivalent iron lines. On the basis of the fluorescent yield, it can be concluded that less than one-third of the decays will produce divalent iron, but the observed intensity ratio is significantly greater. We would therefore conclude that the trivalent iron must, to some extent, decay to divalent iron in a time somewhat greater than  $10^{-7}$  sec. The process is analogous to that described above, but the exchange of an electron between a trivalent iron atom and a divalent cobalt atom, which in effect exchanges their valence states, is energetically much less favorable. Such an electron-hopping process which may contribute to the linewidth has been observed in magnetite.<sup>19</sup>

The data taken at 78°K, Fig. 1(d), show a quite different hfs for the divalent iron, while the trivalent iron behaves normally. The spectrum here indicates the presence of strong quadrupole coupling with the axis of the electric field gradient tensor approximately perpendicular to the direction of the magnetic field. The analysis was made in the following way: Six lines were assigned to the central part of the emission spectrum observed in Fig. 1(d); the magnetic field was determined from the ground-state splitting represented by the distance between lines 2 and 4, or that between 3 and 5, which were found to be the same; the excited state hfs was then constructed and compared with a two-parameter family of curves giving the splitting as a function of the angle  $\theta$  between  $H$  and  $V_{zz}$  and of the ratio  $\lambda$  of quadrupole to magnetic hf coupling; a satisfactory fit was found for  $\theta = 90^\circ$  and  $\lambda = 0.35$ , from which the quadrupole coupling and magnetic field were determined. The values obtained are 31 Mc/sec for

the quadrupole coupling and  $1.8 \times 10^5$  oe for the hf field. The internal consistency of this analysis, i.e., the agreement between the magnetic field determined in terms of the ground state moment and in terms of the excited state moment indicates that the six lines as originally assigned represent a proper hf structure.

It should be noted that no such quadrupole coupling is apparent in the spectrum of the trivalent iron. Moreover there is no known change in lattice structure between the temperatures of Figs. 1(c) and 1(d). In other words the observed quadrupole coupling must arise from the behavior of the  $\text{Fe}^{2+}$  ion rather than from the lattice, and may represent a Jahn-Teller distortion. The temperature dependence of this effect has not been investigated in detail.

### CONCLUSIONS

These experiments have given the magnetic fields at the nuclei of both divalent and trivalent atoms located in an identical, almost cubic environment. The values obtained are  $2.0 \times 10^5$  oe for  $\text{Fe}^{2+}$  and  $5.6 \times 10^5$  oe in  $\text{Fe}^{3+}$ , both at 0°K. They have also shown that the after-effects of electron capture in a dielectric medium may produce a number of stable charge states having distinct hyperfine structures which may complicate the interpretation of Mössbauer effect data.

### ACKNOWLEDGMENTS

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