

130. Surface Adsorption of ^{57}Co - ^{57}Fe on Iron(II) and Cobalt(II) Oxalates.

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The Mössbauer spectra of sources prepared by adsorption of ^{57}Co - ^{57}Fe on surfaces of iron(II) and cobalt(II) oxalate were compared with those obtained when the solids were (a) co-precipitated with these radionuclides and (b) used as absorbers with a monochromatic ^{57}Co - ^{57}Fe source. Some 40% of the adsorbed iron atoms were strongly held on the surfaces in positions which did not appear to be chemically very different from the normal positions in the lattices of those solids. However, when iron(II) oxalate was heated at its temperature of decomposition, the characteristic resonance lines weakened and became unobservable.

THE nature of the chemical environment of ions adsorbed on the surface of a solid is difficult to investigate by conventional methods. An adsorbed ion may be held in a diffuse electric double layer¹ or may occupy a specific lattice site.² We here present an experimental method by which these two alternative methods of bonding may be distinguished, and data on the behaviour of atoms on the surface of a solid which may be obtained by use of this new method.

EXPERIMENTAL

The material investigated was made the source in a Mössbauer assembly³ described elsewhere.⁴ The absorber was a 0.005 in. thick piece of non-magnetic stainless steel (12% chromium) which moved relative to the source. Sources were made by precipitating either iron(II) or cobalt(II) oxalate from 60 ml. of a 0.1M-solution of oxalic acid (adjusted to a pH of 5.00 by addition of dilute ammonia solution) by adding 0.1M-solutions of iron(II) ammonium sulphate or cobalt(II) sulphate. After precipitation, about 0.5 millicurie of ^{57}Co - ^{57}Fe mixture was added in 0.5 ml. of solution, and the vessel agitated. Sources 1—5, 8, and 9 were all prepared in this way, the only difference between them being the length of time during which the supernatant liquor was allowed to remain in contact with the precipitate before centrifugation. About 50 mg. each of sources 6, 7, and 10 were prepared by addition of fresh precipitants to the supernatant liquors remaining from the precipitations of sources 3, 6, and 9, respectively. In all cases the precipitates were centrifuged, washed with acetone (0.5 ml.), and allowed to dry on filter paper in the air for about 2 hr. The sources were then mounted in aluminium holders with thin mica windows (less than 0.5 mg./cm.² thick), so that a pellet approximately $\frac{3}{8}$ in. in diameter and $\frac{1}{8}$ in. thick was positioned axially with respect to the scintillation detector. The Mössbauer spectra were determined with the stainless-steel absorber moving axially at velocities up to ± 0.3 cm./sec.⁴ Several of the sources were heated in air between spectral determinations after removal from the Mössbauer apparatus, but without dismantling the source mount.

RESULTS AND DISCUSSION

(a) *Quality of Results.*—Typical spectra are shown in the Figure. With the primary sources the resonance absorption was marked, so that there is no doubt the conclusions drawn below are reliable, but pretreatment of the precipitates often induced chemical changes which resulted in less satisfactory spectra. Indeed, sometimes the resonance absorption was only slightly greater than statistical fluctuation, and it was difficult to be sure that the observed absorption peaks were real (*e.g.*, source 2, Fig.). Nevertheless, evaluation of the chemical shift, δ , proportional to the electron density at the iron nucleus; ΔE_Q , the quadrupole interaction (which provides information on the field gradient at the iron nucleus); and the resonance intensity (related to the strength of binding of the iron

¹ Verwey, *Chem. Rev.*, 1935, **16**, 363.

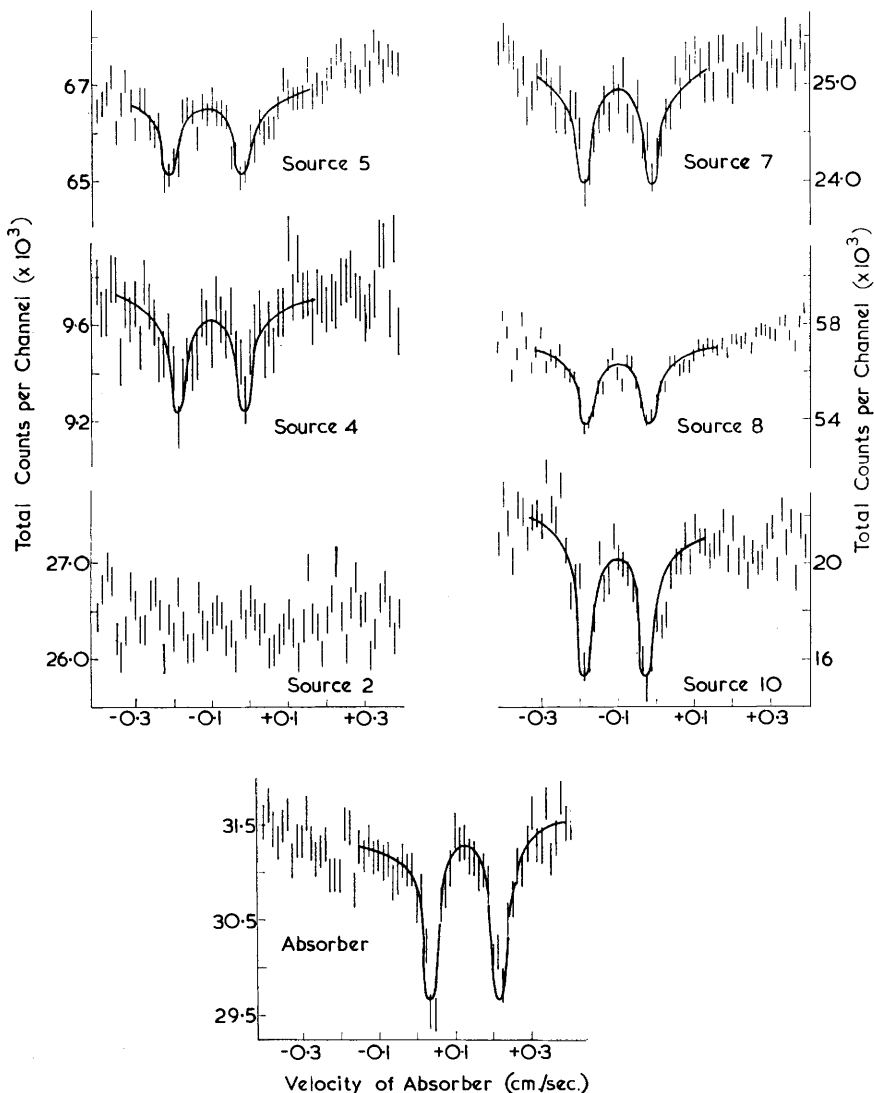
² Paneth and Vorwerk, *Z. physik. Chem.*, 1922, **101**, 445.

³ Mössbauer, *Z. Phys.*, 1959, **151**, 124.

⁴ Brady, Wigley, and Duncan, *Rev. Pure Appl. Chem. (Australia)*, 1962, **12**, 165.

atom) allows useful conclusions to be drawn about the state of the adsorbed species on these surfaces.

(b) *General Features.* We first discuss the results obtained with iron(II) oxalate as absorber. With respect to a natural iron source, this gives $^4\Delta E_Q = 0.17 \pm 0.01$ and $\delta = 0.125$



Mössbauer spectra for sources 2 (after being heated at 260°), 4, 5 (unheated), and 7 [all of iron(II) oxalate]; for sources 8 and 10 [both cobalt(II) oxalate]; and for an iron(II) oxalate absorber used in conjunction with a single-line source (sign reversed). The uncertainty due to statistical variation of counting is shown by the error bars which indicate $\pm\sigma$, where σ is the standard deviation.

± 0.005 cm./sec., which is typical of a spin-free iron(II) compound. The latter indicates an s-electron density at the iron nucleus almost the same as in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, for which the δ -values are, respectively, 0.13 ± 0.05 ,⁴ 0.13 ,⁵ and 0.13 ± 0.004 ⁴ cm./sec. However, the quadrupole interactions suggest a rather

⁵ DeBenedetti, Lang, and Ingalls, *Phys. Rev. Letters*, 1961, **6**, 60.

smaller electronic anisotropy than is usual with typical ionic ferrous compounds (*e.g.*, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 0.300; $^5 \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.315 ± 0.01 ; 4 although it appears to be not greatly different from that in $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.175 ± 0.005 4). Iron(II) oxalate is therefore a spin-free compound, with some interactions between the iron(II) ion and the asymmetrically arranged oxalate groups. Although it could not have been theoretically predicted, Mössbauer spectra show 4 that the same is true of iron(III) oxalate ($\Delta E_Q = 0.05 \pm 0.007$, $\delta = 0.045 \pm 0.005$), and ammonium trioxalatoferrate(III) ($\Delta E_Q < 0.10$, $\delta = 0.035 \pm 0.005$). Magnetic evidence 6 shows potassium trioxalatoferrate(III), to be a spin-free complex, bound by use of $4d$ electrons, in agreement with the findings from Mössbauer spectra.

Results for iron(II) and cobalt(II) oxalate.
Velocities for resonance absorption (cm./sec.)

Ref.	Heating		Iron(II) oxalate sources							ΔE_Q	δ	$1 - (I/I_0)$	
	Temp. (°c)	Time (hr.)	1	2	3	4	5	6	7				
a	Room	—	-0.24 -0.04					-0.20 -0.02			0.18	0.11	0.022
a	80	146			-0.19 -0.06							0.20	0.14
a	120	27		-0.20 -0.02 -0.19 -0.02							0.13	0.13	0.026
a	120	27									0.18	0.11	0.026
b	130	115			-0.17 -0.04						0.17	0.11	0.022
b	130	115									0.13	0.11	0.025
c	130	115				-0.19 -0.03 -0.19 -0.03					0.16	0.11	0.026
c	130	115									0.16	0.11	0.045
a	148	91		none									0.00
a	240	48						none					0.00
a	260	95		none									0.00
d	130	115						-0.20 -0.03 -0.20 -0.01			0.17	0.12	0.016
d	130	115									0.19	0.11	0.041
e	130	115							-0.20 -0.01 -0.19 -0.01		0.19	0.11	0.035
e	130	115									0.18	0.10	0.044
Cobalt(II) oxalate sources													
				8	9	10							
f	130	115		-0.20 -0.19	-0.03 -0.02						0.17	0.12	0.032
f	130	115									0.17	0.11	0.032
g	130	115				-0.19	-0.03				0.16	0.11	0.046
h	130	115						-0.18	-0.02		0.16	0.10	0.021

(a) Iron(II) oxalate centrifuged as soon as carrier added. (b) Iron(II) oxalate kept for 2 min. before centrifugation after carrier added. (c) Iron(II) oxalate kept for 30 min. before centrifugation after carrier added. (d) Iron(II) oxalate precipitated from supernatant liquid from source 3 preparation by addition of 50 mg. each of anhydrous iron(II) sulphate and oxalic acid dihydrate. (e) As (d) except that precipitate was left for 48 hr. before centrifugation. (f) Precipitate centrifuged 2 min. after precipitation. (g) Precipitate centrifuged 30 min. after precipitation. (h) Cobalt(II) oxalate was precipitated from the supernatant liquid from the preparation of source 9 by addition of 20 mg. each of cobalt(II) sulphate hydrate and oxalic acid dihydrate.

The intensities of the resonance lines in Mössbauer spectra are dependent on the Debye temperature and the Debye-Waller factor. 7 Corrections for resonant and non-resonant self-absorption losses in different sources must be made before these parameters can be

6 Selwood, "Magnetochemistry," Interscience, New York, 1936.

7 Lipkin, *Ann. Physics*, 1960, **9**, 332.

evaluated, and such calculations become imprecise when the source thickness is large. In addition, from a chemical viewpoint, evaluation of an effective Debye temperature is of little significance, since Debye theory only applies to the simplest crystalline solids. For this reason, spectra should be compared so far as possible in cases where the number of iron-57 nuclei (resonant absorption) and the total mass (non-resonant absorption) per unit area are sensibly constant. In the case of the cobalt(II) oxalate sources, the concentration of iron-57 is effectively zero, so that in these sources only non-resonant scattering processes are significant. As expected, the line-widths for such sources of similar thickness are almost the same (± 0.005 cm./sec.). Even for both types of source, the line-width was found to be between 0.05 ± 0.01 cm./sec., compared with an experimental line-width of 0.042 cm./sec. for $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$. To a reasonable approximation, therefore the peak depth, equal to the ratio $1 - (I/I_0)$ where I is the peak intensity and I_0 is the intensity out of resonance, is a measure of the frequency of recoilless γ -emission. Increase in this ratio indicates that a greater proportion of the emitting atoms is firmly bound to the environment, and *vice versa*. Since $1 - (I/I_0)$ could not be obtained to better than ± 0.01 , and this parameter is not sensitive to changes in chemical binding energy, only semiquantitative conclusions have been drawn about the environment of the emitting atoms from the intensities of the resonance lines. These afford satisfying confirmation of the more detailed conclusions based on ΔE_Q and δ values given later.

When iron-57 is incorporated in unheated iron(II) oxalate as a source, good Mössbauer spectra are obtained (see Table) similar to those found when this compound is used as absorber [$1 - (I/I_0) = 0.055$]. This shows that the absorbed ions are held in sites of energy which is sufficiently high to preclude energy loss of the emitted radiation by recoil. We calculate that the proportion which are thus held in sources 1–4 is high, often greater than 40%. Thus a large proportion of the adsorbed ions cannot be held on these superficially dried surfaces in diffuse electric double layers.

The electron density at an iron nucleus in the body of iron(II) oxalate, as judged by the emission spectrum of source 6, corresponds to $\delta = 0.123 \pm 0.01$ cm./sec., which is identical, within experimental error, with that estimated from the absorption spectrum of inactive iron(II) oxalate. Indeed, almost all the sources, whether heated or not, have δ -values which agree with the value, 0.125 cm./sec., expected for an iron(II) atom in the solid oxalate. This similarity of δ (and ΔE_Q , see next paragraph) for this compound when used as source and absorber, suggests that the decay process itself usually has little chemical significance [however, see paragraph (e)], by contrast with the observation of Wertheim⁸ that the electronic state after decay was different from that beforehand in the case of cobalt(II) oxide.

The values of ΔE_Q for iron(II) oxalate sources range between 0.13 and 0.20 cm./sec. and are to be compared with 0.17 ± 0.01 cm./sec. as absorber. There is thus clearly some variability in the field gradient at the iron nucleus in the surface-prepared sources. But such a small difference would hardly be possible if the Mössbauer atoms of the surface-prepared sources were chemically bound on one side only. It follows, therefore, that a counter anion, or another species (such as water) is adsorbed on top of the surface-held radioactive iron(II) ions. Indeed, the close similarity of δ and ΔE_Q strongly suggests that the other species is another oxalate ion—*i.e.*, that continuous recrystallisation is occurring at the surface, and that the parent cobalt(II) ions are incorporated in the iron(II) oxalate lattice very close to, but below, the surface by an exchange reaction. A similar interpretation has been given of the kinetics of radioactive surface exchange reactions.^{9,10}

(c) *Contact with Supernatant Solution.*—The above conclusion is confirmed by studying the spectra after the precipitate had been kept in contact with the supernatant solution. The precipitates increased in activity by about 100% on being kept for 30 min. before

⁸ Wertheim, *Phys. Rev.*, 1961, **124**, 764.

⁹ Doerner and Hoskins, *J. Amer. Chem. Soc.*, 1925, **47**, 662.

¹⁰ Langer, *J. Chem. Phys.*, 1942, **10**, 321.

filtration, compared with filtration immediately after precipitation, but no significant change was observable in the resulting Mössbauer spectra or in the fraction of decays leading to recoilless transitions (see Table).

(d) *Change in the Chemical Nature of the Precipitate.*—There appears to be only a small difference between the spectra of cobalt(II) and iron(II) oxalate (see Table). The values of δ and ΔE_Q are hardly distinguishable experimentally. This result requires a very similar arrangement of the oxalate radicals about the decaying atoms in the two cases. A similar crystalline structure is not unreasonable, however, in view of the close chemical similarity of the two elements, and their similar ionic radii in the divalent state (Co^{2+} , 0.82 Å; Fe^{2+} 0.83 Å). In both solids, the daughter iron atom is detectable mainly in a spin-free iron(II) state, and one therefore expects that it would be bound by similar forces in the two solids. The fraction $1 - (I/I_0)$ shows that in the freshly precipitated sources which had been heated to low temperature, there is no observable difference between the fractions of recoilless transitions. The effective Debye temperatures of the "surface" material in the two cases are therefore comparable, as are the binding energies which are also similar to that in the body of iron(II) oxalate. There is a small variation in $1 - (I/I_0)$ with different pretreatments but not enough to be significant until decomposition ensues [in the case of the iron(II) oxalate], when I/I_0 becomes unity.

(e) *Changes induced by Heat.*—Despite their general similarity, there is evidence of minor differences between several of these sources. Thus, there appear to be several subsidiary resonances, just outside experimental error, especially at -0.10 cm./sec. in the heated compounds. If real, these are unlikely to be due to magnetic splitting, since neither of the oxalates is ferromagnetic. It is true that there is the possibility of formation of ferromagnetic Fe_2O_3 in the iron(II) oxalates, but weight changes did not indicate any substantial decomposition until heating was extended to 148° for 91 hr. (sources 5 and 2; see Table 1). The weight change was then in almost quantitative agreement with that expected for formation of Fe_2O_3 from $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The resulting spectrum (similar to source 2, heated to 270° ; see Fig.) did not however, show any clear-cut ferromagnetic splitting (6 resonances) as expected for this compound.⁸ We conclude, therefore, that although decomposition occurred, the thermal energy at this temperature was much lower than the activation energy required for migration of the active material into the lattice sites of Fe_2O_3 even at 270° . Any pronounced unusual resonances in specimens heated at lower temperatures must therefore be due to other causes. The most likely reason for appearance of a peak at -0.10 cm./sec. is oxidation of some of the radioactive atoms on the surface of the solid to the trivalent state, so that a spin-free iron(III) resonance appears (expected for sources at δ from -0.03 to -0.10 cm./sec.), either by atmospheric oxidation or by oxidation during the radioactive decay itself as a consequence of the K -capture [as observed by Wertheim¹¹ for cobalt(II) oxide]. This peak is just detectable in the spectrum of the unheated iron(II) oxalate source and appears in those of the heated cobalt(II) and heated iron(II) oxalate. It would appear therefore to be an essential consequence of the radioactive process in some of the decays. It is, however, not possible to say whether the low frequency with which this resonance occurs is affected primarily by oxidation in the K -shell of the emitting atom itself or of the surface environment in which it finds itself.

Conclusions.—This method can give useful information about the behaviour of absorbed material on the surfaces of solids. With these solids, a large proportion of the active material is found in sites that are very similar in chemical environment (field gradient and electron density) to those present in the lattice of normal iron(II) oxalate. Neither heating to temperatures below the decomposition point nor use of longer times of equilibration between the solid and the solution from which it is formed greatly affects the type of lattice site occupied, except that a small proportion of the atoms appear to be formed in an electronically impoverished condition.

¹¹ Wertheim, *J. Appl. Phys.*, 1961, **32**, 1105; Kistner and Sunyar, *Phys. Rev. Letters*, 1960, **4**, 412.

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