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Mössbauer, X-ray, and Chemical Studies
of Cobaltous Oxide

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*This report is based on a thesis submitted for the degree of Doctor of Philosophy at Purdue University.

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Symbol	Name	Page
f	Recoil-free fraction	52
θ_M	Mössbauer Debye temperature.	52
F_{hkl}	Crystal structure factor ($h, k, l \equiv$ Miller indices).	63
$\mathcal{H}_e$	Hamiltonian for the combined magnetic hyperfine and electric quadrupole in- teraction.	67
$\vec{I}$	Nuclear spin operator.	67
μ_N	Nuclear magneton	67
$\vec{H}$	Magnetic hyperfine field at a nucleus. . .	67
$V_{x'x'}, V_{y'y'}, V_{z'z'}$	Principal values of the electric field gradient (EFG) tensor.	67
eq	Electric field gradient along the prin- cipal axis having the maximum EFG.	67
η	Asymmetry parameter of the EFG	67
θ, ϕ	Polar and azimuthal angle of $\vec{H}$ with respect to the principal axes of EFG . . .	67
Q	Nuclear quadrupole moment of the first excited state of Fe^{57} multiplied by the Sternheimer factor	67
g_1, g_0	Absolute values of the g-factors of the first excited state and the ground state of Fe^{57}	67, 71
P	$e^2 qQ/6g_1\mu_N H$	68
ψ_i	Orbital wave functions of the d_e state . .	77

Symbol		Page
χ_j	Spin wave functions for $S=2$	77
λ	Spin-orbit coupling constant	78
α^2	Covalency factor	79
$\vec{L}$	Orbital angular momentum	77
$\vec{S}$	Spin angular momentum.	78
$\vec{l}$	Pseudoangular momentum	77
Δ	Proportionality constant of tetra- gonal distortion of CoO(I)	78
$\vec{M}$	Unit vector in the molecular-field direction.	79
μ_B	Bohr magneton.	80
$\mathcal{H}'$	Perturbation Hamiltonian which removes the degeneracy of the d_e level	78
θ_o	Polar angle of the Co^{+2} spin direc- tion relative to crystal c-axis.	78
β	Molecular field constant	79
$\langle S_i \rangle$	Statistical average of Co^{+2} spin.	79
x	$\beta \langle S_i \rangle$	134
ψ_m	Wave functions of the d_e state in the absence of $\mathcal{H}'$	79
E_n	Eigenenergies due to $\mathcal{H}'$	79
ϕ_n	Eigenfunctions corresponding to E_n	79
a_{mn}	Unitary matrix elements transforming ψ_m to ϕ_n	79
$\vec{H}_L$	Magnetic hyperfine field produced by the orbital magnetic moment on the parent atom.	80
$\vec{H}_S$	Magnetic hyperfine field produced by the s-electron spin density at the nucleus.	80

Symbol		Page
$\vec{H}_D$	Magnetic hyperfine field produced by the dipolar interaction with the spin moment on the parent atom	81
V_{ij}	Electric field gradient tensor components	83
$\vec{h}_D$	Angular and spin part of $\vec{H}_D$	81
v_{ij}	Angular part of V_{ij}	139

ABSTRACT

Ok, Hang Nam. Ph.D., Purdue University, January 1968. Mössbauer, X-ray, and Chemical Studies of Cobaltous Oxide. Major Professor: James G. Mullen.

The existence of two forms of cobaltous oxide CoO(I) and CoO(II) , has been established by Mössbauer, x-ray, and chemical techniques. CoO(I) has the NaCl structure as determined by a well resolved powder x-ray patterns. Its density is measured to be 6.4 g/cm^3 from both x-ray and direct macroscopic experiments. Fe^{57} Mössbauer lines in CoO(I) , doped with Co^{57} , show only Fe^{2+} when determined by either the isomer shift or the hyperfine splitting below the Néel temperature. We find a Néel temperature of 288°K , which is 3°K less than the value reported by earlier workers. CoO(I) is completely inert in air at room temperature and its stoichiometry does not change over time intervals as long as two months. CoO(II) could be prepared at low temperatures only. Form II also had the NaCl structure but the x-ray line of the powder pattern was very broad. The density of CoO(II) is $3.2 \pm \frac{1.0}{0.0} \text{ g/cm}^3$, about half of the value found for CoO(I) . CoO(II) shows only Fe^{3+} lines in the Mössbauer pattern, with the appropriate isomer shift and hyperfine field. CoO(II) is very reactive with oxygen, at room temperature, although the x-ray pattern is not appreciably altered after oxygen absorption. CoO(II) has a Néel temperature of $270^\circ\text{K} \pm 10^\circ\text{K}$, slightly less than CoO(I) , and an effective

Mössbauer characteristic temperature of 320°K , substantially less than the 510°K found for CoO(I) . The results of studies of thermally activated transformation of $\text{II} \rightarrow \text{I}$ and pressure and quenching experiments are given. CoO(I, II) , a mixture of forms I and II is obtained by the usual chemical recipes. This mixed material was also studied. At low temperature CoO(I, II) behaves as a simple mixture of I and II, but at temperatures above 200°K there is an interplay between the two forms, which is responsible for the observed increase in the relative fraction of Fe^{3+} to Fe^{2+} observed in the Mössbauer patterns. This interplay is also connected with the shift in the apparent Néel temperature for Fe^{3+} in pure form II compared with the value obtained for CoO(I, II) . A detailed model is proposed which explains all of the properties observed thus far. The data preclude the possibility of Auger aftereffects in cobaltous oxide, as suggested by Wertheim, and they also show that stoichiometry fluctuations are not the principal cause of the observed Fe^{3+} Mössbauer line, as was recently claimed by Triftshäuser and Craig. The hyperfine spectra of CoO(I) below the Néel temperature give a pattern characteristic of magnetic and quadrupole hyperfine interactions. They are analyzed by diagonalizing a 4×4 magnetic and quadrupole interaction matrix of the first excited state of an Fe^{57} nucleus and fitting eight Lorentzians to the Mössbauer spectra. In connection with this analysis we have developed a general formalism which can give H , $e^2qQ/2$, ϕ , θ , and η from Mössbauer data by using an IBM computer. Below 200°K the magnetic hyperfine field at Fe^{57} nuclei in CoO(I) decreases with decreasing temperature, and has an internal field of magnitude 120 kG

as its zero-point value. The quadrupole interaction increases with decreasing temperature, and the zero-point value of $e^2qQ/2$ is -1.32 mm/sec for CoO(I) . The tendency of the magnetic hyperfine field to decrease and the tendency of the quadrupole interaction to increase with decreasing temperature, as well as the temperature dependence of θ , ϕ , and η can be explained by crystal field theory in terms of temperature-dependent variations in the statistical population of electronic levels. The hyperfine Mössbauer spectra of CoO(II) below its Néel temperature consist of six lines, which are purely magnetic except for line broadening due to possible quadrupole interactions arising from defects which destroy long ranged translational symmetry in this material. The zero-point value of the magnetic hyperfine field at Fe^{57} nuclei in CoO(II) is measured to be 553 kG. The temperature dependence of the magnetic hyperfine field for CoO(II) follows a Brillouin function for $S = 3/2$ approximately. The Mössbauer hyperfine spectra of the mixed form, CoO(I, II) , was also determined. The magnetic hyperfine field and quadrupole coupling constant for the Fe^{2+} component of the Mössbauer spectra are found to be 150 kG and -1.01 mm/sec at 77°K , respectively, which are not in accord with the previously reported values by Wertheim. Hydrated cobaltous chlorides were also studied in connection with Auger aftereffects. No evidence for Auger aftereffects is found in these materials, and the similarity of Mössbauer spectra for $\text{CoCl}_2 \cdot n\text{H}_2\text{O}$ ($n = 2, 4, 6$) can be explained by postulating recoil aftereffects associated with neutrino emission following K-capture by Co^{57} .

I. INTRODUCTION

Before 1958, the observation of resonantly scattered or absorbed nuclear gamma-rays was difficult because the natural width of nuclear isomeric states is almost always small compared to the energy of the recoiling nucleus. One way to compensate for the recoil energy loss is to spin the source on a high-speed rotor, to Doppler shift the emitted gamma rays. ($10^4 \sim 10^5$ cm/sec for a typical case). Another method involves raising the temperatures of the source and absorber (or scatterer), to Doppler broaden the gamma spectra. A third method utilizes the velocity which may be imparted to an atom by a preceding nuclear decay or particle reaction. A remarkable new method was discovered by Mössbauer¹ in 1958. His method is different in principle from those preceding it, in that the emitting (or absorbing) nucleus does not recoil. This is accomplished simply by having the nuclei bound in a solid at low temperature. When a gamma-ray is emitted or absorbed by such a nucleus, the recoil momentum is taken up under a certain condition by the whole crystal, with no energy transferred to internal excitations of the lattice, because the lattice is a quantized system which cannot be excited in an arbitrary fashion. When the lattice is not excited the widths of the nuclear levels involved in the transitions alone determine the linewidth of the zero-phonon gamma ray. According to the uncertainty principle, a nuclear

lifetime of 10^{-7} sec corresponds to a width of $\sim 10^{-8}$ eV, which is smaller than the characteristic energy values for the magnetic hyperfine and electric quadrupole interactions of nuclei with their surrounding electrons. Therefore, these interactions could in principle be observed and studied through the Mössbauer effect. The narrowness of the linewidth of a Mössbauer line (zero-phonon line) also makes it possible to detect a shift in nuclear levels which arise from a Coulomb interaction of the nuclear charge with the s-electron charge cloud. A change in the s-electron density such as might arise from a change in valence will result in a shift of Mössbauer lines, which is very useful in studying multiple charge states of ions in solids. The nucleus most commonly used in Mössbauer studies is Fe^{57} , whose parent, Co^{57} , decays by electron capture in accordance with the decay scheme shown in Fig. 1. The half-life of the 14.4 keV level is 10^{-7} sec, and its decay is either through internal conversion (internal conversion coefficient $\alpha = 9$), or by the emission of a 14.4 keV gamma ray, which is used for Mössbauer studies. Right after electron capture by Co^{57} the newly formed Fe^{57} ion has the electronic structure of Co^{57} with an inner electron missing. The resulting inner hole (most probably a K-electron hole) is filled by an outer electron, with the emission of either an x-ray or an Auger electron. These processes continue until the valence electrons are reached. Each time an Auger process takes place, the charge state of the atom is increased by one. Therefore, highly charged states occur after an Auger cascade. Following such a cascade the charged ions will capture electrons until electronic equilibrium is achieved. In metals,

Fig. 1. The decay of Co⁵⁷ to Fe⁵⁷.

both the Auger cascade and the final capture process take place in a time short compared to 10^{-7} sec, because there is an abundance of conduction electrons in metals. In a dielectric material it is questionable whether the decaying Fe^{57} ion is in complete charge equilibrium with its surroundings in a time short compared to 10^{-7} sec, the half-life of the first excited state of Fe^{57} . The first Mössbauer experiment which discussed this problem was that of Wertheim² using a sample of CoO . At room temperature, two partially resolved lines were found which were identified as arising from $+2$ and $+3$ charge states. Two sets of hyperfine split lines at low temperatures confirmed the room-temperature identification of the charge states. The existence of the two charge states was interpreted by Wertheim as evidence that the time required to reach electronic charge equilibrium, following the emission of Auger electrons, can be of the order of or greater than the half-life of the first excited state of the nucleus Fe^{57} (10^{-7} sec). On the basis of Wertheim's results Pollak³ concluded that an Auger cascade could produce about 5% Fe^{2+} and 95% Fe^{3+} very rapidly, and the mean life of the Fe^{3+} in CoO at room temperature should be 1.4×10^{-7} sec. Bhide and Shenoy⁴ confirmed Wertheim's results, which were taken over the temperature range between 77°K and 298°K , and extended the experiment above room temperature to about 1000°K . They also observed an increase in the intensity of Fe^{3+} with increasing temperature, which was attributed to a monotonic increase in the relaxation time of Fe^{3+} as the temperature increased. Since Wertheim reported the observation of two charge states in Mössbauer studies on cobaltous oxide, other observations

have been made⁶⁻⁸, which have been interpreted as further evidence that in some materials the time required to reach electronic equilibrium, following the emission of Auger electrons, can be comparable to 10^{-7} sec.

We already reported⁵ the results of our studies on CoO, which indicate no evidence for Auger aftereffects. Studies on many chemically simple materials such as CoCl_2 and CoI_2 also gave no evidence for Auger aftereffects^{9,10}. For $\text{CoCl}_2 \cdot n\text{H}_2\text{O}$ ($n=0, 2, 4, 6$), no evidence for Auger aftereffects is found in the present work, which will be described in Appendix D in connection with recoil aftereffects. A form of cobaltous oxide which showed an Fe^{3+} Mössbauer pattern without any Fe^{2+} pattern, was prepared, and our results indicated that the experiment of Wertheim resulted from two distinct forms of cobaltous oxide. Form I showed only Fe^{2+} lines, while form II showed only Fe^{3+} lines.

At almost the same time and independently Triftshäuser and Craig¹¹ reported no evidence for Auger aftereffects in CoO, using the time delay technique, although they suggested, in contrast to our own proposal, that the observed Fe^{3+} charge state could be interpreted in terms of a small excess of cation vacancies in CoO, associated with imperfect stoichiometry. This model will be subsequently referred to as the TC (Triftshäuser and Craig) model. Their proposal of cation vacancies was mainly based on the electrical conductivity measurement on polycrystalline cobaltous oxide by Fisher and Tannhäuser¹². Using the x-ray diffraction patterns which showed no diffraction rings not ascribable to CoO Triftshäuser and Craig concluded that their sample

was perfect, except for a possible small number of cation (+) vacancies. We already pointed out⁵ that their x-ray determination was inconclusive, and this point will be discussed fully in a later section of this thesis, where we give in detail the results of our own x-ray studies. We also reported that the form II, CoO, converted irreversibly to the form I on heating in an inert atmosphere at elevated temperatures. This observation was in contradiction to the claims of Triftshäuser and Craig, who asserted that the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ was completely reversible on temperature cycling. Although we communicated our results to Craig¹³, and these results are quoted in some detail in the recent publication by Triftshäuser and Craig¹⁴, it should be emphasized that there is a basic conflict between our results and their conclusions. Although variations in stoichiometries of CoO are possible, particularly for CoO(II), our results indicate that this is not the underlying reason why Fe^{2+} and Fe^{3+} (those corresponding to CoO(I) and CoO(II)) are observed in Mössbauer source experiments using cobaltous oxide.

We will present in detail the results of our recent studies on cobaltous oxide, and show that these results can be explained neither by Auger aftereffects, nor by the TC model, but require a model based on the existence of two distinct forms of cobaltous oxide, which we will subsequently refer to as CoO(I) and CoO(II). Our data indicate that CoO(I) has the complete NaCl structure with no vacancies and shows only Fe^{2+} lines in its Mössbauer spectra, while CoO(II) has an NaCl structure with half of the lattice sites vacant and shows only Fe^{3+} lines in its Mössbauer spectra. We were able to isolate CoO(I)

and CoO(II) completely, so that the postulation, of Auger after-effects was unnecessary. Our density measurements showed that the density of CoO(II) was only half of that of CoO(I) , which strongly supports our model and rules out the TC model because that model would only be consistent with small variations in density associated with small concentrations of cation vacancies. We will attempt to show that the model which we had proposed earlier⁵, is indeed, correct, and we will elaborate upon this model. Bizette¹⁵ and La Blanchetais¹⁶ reported that cobaltous oxide is an antiferromagnetic substance with a Néel temperature, T_N , of 291°K . According to Tombs and Rooksby's x-ray measurements¹⁷, the crystal structure of the cobaltous oxide is strictly of the NaCl type ($a_0 = 4.25 \text{ \AA}$ at 20°C), whereas below T_N the lattice undergoes a slight contraction along the c-axis, which increases gradually with decreasing temperature. Their results indicate that

$$\frac{c}{a} = 0.995 \quad \text{at} \quad 203^\circ\text{K},$$

and

$$\frac{c}{a} = 0.988 \quad \text{at} \quad 93^\circ\text{K}.$$

Saito, Nakahigashi, and Shimomura¹⁸ show that

$$\frac{c}{a} = 0.988 \quad \text{at} \quad 123^\circ\text{K},$$

and they report a new rhombohedral deformation in addition to the well known tetragonal deformation. From neutron diffraction data

Roth¹⁹ claimed that the spin direction for CoO is $[\bar{1}\bar{1}7]$, a direction which makes an angle of $11^{\circ}31'$ with respect to $[001]$. Using a high-resolution neutron diffractometer van Laar²⁰ finds that his experimental results can be explained by either of the following two models: a) a collinear rhombohedral spin arrangement with an angle between the c-axis and the spin axis of 27.4° ; b) a multispin-axis tetragonal arrangement, consisting of four antiferromagnetic sublattices with different spin axes which also make an angle of 27.4° with respect to the c-axis. He suggested that model b) was preferable because CoO deforms tetragonally below its Néel temperature. The multispin axis model was denied, however, by Nagamiya, Saito, Shimomura and Uchida²¹, and also by Saito, Nakahigashi and Shimomura¹⁸, who found a rhombohedral elongation, specified by the off-diagonal strain tensor components $e_{yz} = e_{zx} = e_{xy}$ of magnitude 5×10^{-4} .

Mössbauer spectra of CoO(I) taken below the Néel point show a splitting due to the magnetic hyperfine interaction and quadrupole interaction at the Fe^{57} nucleus. The temperature dependence of the magnetic hyperfine field at Fe^{57} nuclei in CoO(I) has a maximum at about 180°K and then decreases monotonically with decreasing temperature, while the temperature dependence of the quadrupole interaction increases monotonically as the temperature decreases. A similar result was reported by Siegwarth²² for divalent Fe^{57} in NiO. The tendency for the magnetic hyperfine field to decrease and the quadrupole interaction to increase with decreasing temperature at Fe^{57} nuclei in CoO(I) can be explained in terms of a statistical variation in the

population of perturbed electronic levels under the spin-orbit coupling, the exchange interaction, and the effect of crystal distortion. Mössbauer spectra of CoO(II) taken below the Néel temperature show six-line magnetic hyperfine patterns characteristic of Fe^{3+} .

The magnetic hyperfine field was found to follow a Brillouin function only to a rough approximation. Mössbauer spectra of CoO(I, II) consist of two sets of hyperfine patterns below the Néel temperature, one corresponding to Fe^{2+} and the other corresponding to Fe^{3+} . The hyperfine patterns of Fe^{2+} in CoO(I, II) are exactly the same as those of pure CoO(I), while those of Fe^{3+} in CoO(I, II) are almost the same as those of pure CoO(II) at low temperatures, but have a higher Néel temperature than that of pure CoO(II).

II. EXPERIMENTAL TECHNIQUES

A. Method of Mössbauer Spectrometry

Our method of velocity spectrometry has been described earlier⁹. The Mössbauer resonances were observed using a mechanical velocity spectrometer, which produced a crank motion at the absorber. A schematic drawing of this mechanical system and the associated electronics is shown in Fig. 2. The synchronous motor and 100:1 gear reducer were mounted on a separate table from the crank assembly and power was transferred to the crank via an elastic belt (made by Tilton Company). Various combinations of pulleys (concentric to 0.0002 in) gave various ranges of velocities. A large flywheel was attached to the crank to prevent any loss of synchronism between the motor and the crank assembly. Velocities of rotation of the flywheel were directly measured to be uniform within 0.5%. While the absorber executed a continuous reciprocating crank motion in time, gamma rays from Fe^{57} nuclei were analyzed with a gas-filled proportional counter, a preamplifier, and a single-channel analyzer. The pulses from the 14.4 keV gamma rays were then sent into a 400-channel RIDL multichannel analyzer, which was operated as a multichannel scaler, with the channel address being advanced linearly in time, via an independent oscillator. The analyzer system was reset synchronously with the reciprocating motion by a pulse generated from a photodiode.

Fig. 2. Schematic diagram of the spectrometer.

Synchronism in the reset was held to 0.01 channels by operating the sine wave oscillator at 100 times the channel-stepping frequency. This frequency attenuation was accomplished with two scaler units in series. After a reset pulse, the first fast oscillator pulse sent into the "divide by 100" unit was random to within one cycle of the fast oscillator or to 0.01 channels. Because of this synchronism the 14.4-keV pulses registered in a given channel corresponded to a unique absorber velocity, which was evaluated from the measured parameters of the crank motion. The frequency of rotation of the crank was recorded on each experiment by counting the number of reset pulses generated during the experiment. A 16- μ sec delay circuit was used to avoid any inference between reset and address advance pulses.

Low source temperatures were obtained by attaching the source to a copper block welded to the bottom of a Dewar filled with various coolants. A Mössbauer source could be heated to 750 $^{\circ}$ K by a Watlow heater rod inserted into a hole in the copper block of the Dewar. Source temperatures below 77 $^{\circ}$ K were obtained by attaching the source to a lightweight liquid helium Dewar made by Texas Instrument Co.

Narrow unsplit sodium ferrocyanide absorbers of various effective thicknesses in Fe⁵⁷ (0.5 mg/cm², 0.75 mg/cm², and 1.0 mg/cm²) made by New England Nuclear Corporation were used in this work. Throughout this work the absorbers were kept at room temperature, while the temperatures of the sources were varied.

B. Sample Preparation

We found two methods for preparing the unusual form of cobaltous oxide, CoO(II). This material could be formed either by heating CoCO_3 in high vacuum or by reducing a higher oxide formed from a nitrate in a hydrogen atmosphere at low temperatures.

A radioactive solution of CoCl_2 was mixed with slightly more than two molecular equivalents of NaHCO_3 to produce the following reaction in a CO_2 atmosphere or an argon atmosphere at the boiling point of the mixture:

By removing NaCl by the water dilution method, we could get the radioactive CoCO_3 , which was heated at 300°C in vacuum to give a very dark brown (almost black) material, which had the chemical composition CoO, and is the oxide form which we refer to by the label II. It was necessary to do the chemistry in a glove box (a vacuum glove box made by Sargent Co.) filled with argon gas, because CoO(II) rapidly absorbs oxygen, a property which will be discussed later. The absorption of oxygen by CoO(II) is so noticeable that we spoil a sample of CoO(II) in air unless we enclose it in a leak-proof capsule. Various kinds of capsules were devised to keep CoO(II) samples from being exposed to air during Mössbauer runs, gravimetric measurements, and x-ray determinations. A typical example of the type of capsules used is shown in Fig. 3, which can be used in a gravimetric determination of stoichiometry. The weight of a capsule was minimized by making it from aluminum. A sample of CoO(II) is

Fig. 3. A typical example of vacuum-tight capsules.

prepared usually in a ceramic vial, which is encapsulated in an aluminum capsule with an air-tight, thin, rubber seal.

The hydrogen reduction method was performed in the following way: a sample of cobaltous nitrate was heated at 200°C to produce a higher oxide of cobalt, which was reduced in a hydrogen atmosphere of about 200 mm Hg pressure at about 210°C to give CoO(II) . This method had the limitation that it always gave a small amount of cobalt metal in the reduction process.

CoO(I) can be prepared by heating cobalt metal in a carbon dioxide atmosphere. After reducing Co_3O_4 to Co metal at 800°C - 900°C in a hydrogen atmosphere we oxidized the metal in a carbon dioxide atmosphere at 1000°C in a sealed quartz tube. The CO_2 atmosphere was added after the hydrogen was evacuated. At the high temperatures used CO_2 partially disassociates thereby permitting the oxidation of the cobalt metal. The specimen was quenched in a helium atmosphere from 1000°C to 0°C in an ice bath and to 77°K in a liquid nitrogen bath. The CoO(I) prepared by this method had a light brown color (almost yellow). In preparing a CoO(I) sample it was necessary to change atmosphere frequently in the quartz tube which contained the sample. For this purpose the quartz tube was connected to a vacuum pump, a mercury manometer, and gas tanks. In high temperature annealing a large thermal gradient across the quartz tube in the furnace was possible. In order to eliminate this possibility we placed a solid cylindrical piece of inconel inside the furnace, which was machined to contain the quartz tube and a thermocouple.

CoO(I, II) can be prepared, as most people have done, by heating cobalt metal or cobaltous nitrate at 1000°C in air current and cooling it in an inert atmosphere like argon or nitrogen. The color of CoO prepared in this way was usually dark brown.

C. X-ray Technique

For x-ray diffraction patterns of various samples, a powder x-ray diffractometer made by North American Philips Co. was used along with a Geiger counter and a chart drive. Mo $K\alpha$ lines ($K\alpha_1 = 0.70926$, $K\alpha_2 = 0.71354$) were used with a zirconium filter²³ which strongly absorbed Mo $K\beta$ line and x-rays of wavelengths shorter than $0.687 \text{ \AA}$. The operating voltage and current of the Mo x-ray tube were set at 40 kV and 15 mA, respectively. Simple specimen holders made from plexi-glass like the one illustrated in Fig. 4(a) were used with the powder specimen packed into a $\frac{9}{16}$ -inch dia. circular depression. In this way, the thickness requirement for maximum diffracted intensity²³ was fulfilled for cobalt oxides, namely:

$$t \geq \frac{3.2}{\mu_M} \cdot \frac{\sin \theta}{\rho'}$$

where μ_M is the mass absorption coefficient of the sample, and ρ' is the density of the powder including interstices. For CoO, $\mu_M = 33$ for Mo $K\alpha$, and, taking $\theta = 30^{\circ}$ and $\rho' = 4$, we get $t_{\min} = \frac{1}{80} \text{ cm}$ as the minimum thickness. Therefore the specimen thickness of $\frac{1}{32}$ inch shown in Fig. 4(a) is clearly sufficient for the maximum diffraction intensity. In order to get faithful chart records of the diffraction patterns we used slow scanning speeds ($\frac{1}{8}$ degree per min,

(a)

(b)

Fig. 4. A specimen holder for x-ray diffraction and die for pressure experiments.

$\frac{1}{4}$ degree per min). An incident x-ray beam slit with an angle of beam divergence of 1 degree or $1/12$ degree was used. After being properly amplified the pulses from a Geiger tube were fed into a pulse-averaging circuit which smooth out the pulses into a fluctuating current. This current actuated a chart recorder. The RC time constant of the pulse-averaging circuit was chosen to be 2 sec or 16 sec.

D. Pressure and Quenching Technique

For pressure experiments a die shown in Fig. 4(b) was used. To resist strain due to a high pressure a $1\frac{1}{8}$ inch-thick wall of inconel surrounds the two solid rods with diameters of $\frac{1}{4}$ inch which are made from tool steel. The contacting surfaces of the two rods, between which samples were pressed, were carefully machined to be flat. A hydraulic press machine made by DAKE Corp. was used to achieve the pressure.

For quenching experiments a copper tube with diameter of 1 inch and thickness of 0.05 inches was used to give quick thermal conduction. A sample in the copper tube filled with He gas was quickly quenched in a ice bath and then in a liquid nitrogen bath.

III. PROPOSED MODEL FOR THE STRUCTURE OF COBALTOUS OXIDE

After carrying out extensive studies on cobaltous oxide using standard chemical, Mössbauer, and x-ray techniques, we have evolved the following model. The essence of our model is that there are two distinct types of cobaltous oxide referred to as CoO(I) and CoO(II). While it is possible to isolate these two materials, they are usually combined, when the usual chemical recipes are followed. When they are combined we will refer to the combination CoO(I, II). Combined forms I and II have an interplay which depends on the concentration of II relative to I and on the temperature. In order to simplify the discussion we will enunciate our model, point-by-point, and in subsequent sections we will show how it is in harmony with a wide class of experimental findings, while other proposed models contradict our experimental results. We claim that cobaltous oxide has the structure enumerated in the following:

1. There is a form of CoO, which we call CoO(I), having the NaCl structure with ideal stoichiometry and essentially perfect translational symmetry (Fig. 5(a)). Its density, e.g., is 6.4 g/cm^3 , when measured by either x-ray analysis or a macroscopic density measurement. Mössbauer spectra of CoO(I) show only Fe^{2+} lines.

2. There is a form of CoO, which we will call CoO(II), having the NaCl structure with half of its positive ion sites and half of

Fig. 5

Geometry of different forms as given in proposed model. a) pure form (I) with no vacancies, b) pure form (II) with 50% of its sites vacant. Any long ranged order is less than $50\text{\AA}$. Short-ranged order shown is arbitrary and not intended to show any actual known ordering. c) $\text{CoO(I, II)}_{\text{C}, \text{T}=0}$, a simple mixture of CoO(I) and CoO(II) at 0°K . d) $\text{CoO(I, II)}_{\text{C}, \text{T}}$, anion vacancies are partially dispersed for $T > 200^\circ\text{K}$.

(a) CoO (I)

(b) CoO (II)

(c) $\text{CoO (I, II)}_{\text{C}, T=0}$

(d) $\text{CoO (I, II)}_{\text{C}, T}$
 $T \sim 400^\circ\text{K}$

Fig. 5

its negative ion sites vacant (Fig. 5(b)). While there is no long-ranged order to the vacancy arrangement, there may be and probably is short ranged order (less than $50\text{\AA}$). The density of this material is about 3.2 g/cm^3 and its Mössbauer spectra show only Fe^{3+} .

3. A mixture of CoO(I) and CoO(II) will be denoted generically as CoO(I, II) . At low temperatures (relative concentration of form II = C, temperature = 0) $\text{CoO(I, II)}_{C,0}$ always consists of a simple mixture of CoO(I) and CoO(II) (Fig. 5(c)).

4. At elevated temperatures ($T > 200^\circ\text{K}$) there is an interplay between CoO(I) and CoO(II) , such that the anion vacancies of the form II disperse into the form I lattice (Fig. 5(d)). This interplay is what is responsible for the apparent increase in intensity of Fe^{3+} observed by Bhide and Shenoy⁴, and studied in more detail in the present work. Because the details of this interplay depend on the relative concentrations of form II compared to form I, we refer to it specifically as $\text{CoO(I, II)}_{C,T}$, where C denotes percentage concentration of the form II at $T = 0^\circ\text{K}$, and where T denotes the temperature of the measurement.

IV. MACROSCOPIC PROPERTIES

A. Stoichiometry

The stoichiometries of CoO(I) , CoO(II) , and CoO(I, II) were determined by a combination of gravimetric, x-ray, and Mössbauer measurements. For the preparation of these oxides 99.999% Co and 99.999% HNO_3 were used, and weights were determined by using a Mettler semimicro balance. In order to determine the weight loss due to evaporation we started from cobalt metal and returned to cobalt metal after measuring the weights of CoO . The measured weight losses were within 0.3% of the sample weight. X-ray diffraction patterns were taken to show that these materials had the correct crystal structures (see Section VI for detailed discussion). The form of each specimen was assessed by a Mössbauer measurement. Several measurements showed that all of CoO(I) , CoO(II) , and CoO(I, II) have the chemical composition $\text{CoO}_{1.00 \pm 0.05}$ shown in Table 1. While the values of X for CoO(II) appear slightly greater than one, we believe that this is not significant, as the highly vacated form II gave visible evidence for argon adsorption on the surface.

B. Density

Since CoO(I) has a perfect NaCl structure with a lattice parameter of $a_0 = 4.26 \text{ \AA}$ at 20°C its density should be 6.4 g/cm^3 . In

TABLE 1.

Stoichiometry of cobaltous oxide. Gravimetric determinations of X for basic forms of cobaltous oxide written as CoO_X .

Form Mea- surement	$\text{CoO(II)}^{\text{a)}$	CoO(I, II)	CoO(I)
1	$1.036 \begin{smallmatrix} + 0.010 \\ - 0.050 \end{smallmatrix}$	0.99 ± 0.02	1.02 ± 0.03
2	$1.043 \begin{smallmatrix} + 0.010 \\ - 0.050 \end{smallmatrix}$	0.97 ± 0.03	$1.00 \pm 0.02^{\text{b)}$
3	$1.039 \begin{smallmatrix} + 0.010 \\ - 0.040 \end{smallmatrix}$	0.99 ± 0.05	
4		0.98 ± 0.02	

a) Although these values are slightly greater than one, this was probably the results of argon adsorption as discussed in the text.

b) : A commercial-grade cobalt metal was used for this measurement.

contrast to earlier measurements²⁴ our measurement showed that the density of CoO(I) was $6.4 \pm 0.1 \text{ g/cm}^3$ in excellent accord with the predicted value based on the measured lattice parameter.

On the other hand CoO(II) was found to have a density of about 3.2 g/cm^3 , nearly half of the value found for CoO(I). In Table 2 we list several measured values of the density of CoO(II). Although the inherent difficulties in the measurement are such that a precise value of the density was not possible, we take the best value to be $\rho = 3.2 \pm \begin{smallmatrix} 1.0 \\ 0.0 \end{smallmatrix} \text{ g/cm}^3$, where the lower limit rather than the average value has been chosen on the grounds that the more likely value is the one obtained from low temperature preparation, where the transformation of form II to I was negligible (see Section IV D).

The technique used for the density measurements was the standard volume-gravimetric approach with carbon tetrachloride as a non-reactive liquid in which the various materials were immersed for volume determination by weighing with a Mettler semi-micro balance. For materials which could be prepared in a completely pure form, such as NaCl, Co, etc, the measured densities were within about two percent of the expected values. CoO(II) presented particular problems, however, as the large quantity required for the density measurement ($\sim 3\text{g}$), precluded the possibility of synthesizing the material without some admixture of CoO(I). This was basically because large samples required longer anneals which resulted in the transformation $\text{CoO(II)} \rightarrow \text{CoO(I)}$, a phenomena which was studied in detail and will be described later. Because of this contamination the data given in Table 2 shows the raw values for densities of the actual samples, and

TABLE 2.

Densities of CoO.

Material	Measured density (uncorrected) (g/cm ³)	corrected density (g/cm ³)	temperature of preparation (°C)
CoO(II)	5.7	3.4 ± 0.5	210°
	3.7	3.6 ± 0.5	210°
	4.7	3.3 ± 0.5	210°
	5.6	4.5 + 0.5 - 1.5	300°
	5.1	4.8 + 0.5 - 1.5	300°
CoO(I)	5.1	4.8 + 0.5 - 1.5	300°
	6.38 ± 0.10	6.38 ± 0.10	1000°

values "corrected" for CoO(I) contamination. This correction factor was based on Mössbauer measurements on the same material as used in the density measurements. The errors inherent in the estimate of the correction factor are such that all values are consistent with $\rho_{\text{II}} = 3.2 \text{ g/cm}^3$, but no value of ρ_{II} can be greater than 4.8 g/cm^3 .

Although all macroscopic measurements such as density have their limitations, and can be misleading if not correlated with other experimental evidence, the following additional precautions were taken in an attempt to make the measurement as meaningful as possible.

(1) Powder specimens, which were submerged in Grade "A" volumetric flasks, were pumped with a forevacuum system to eliminate gas bubbles.

(2) It was experimentally verified that CCl_4 did not react with cobaltous oxide by observing the Mössbauer spectrum of a submerged sample.

(3) The experimental determination was repeated several times to check for reproducibility. The results in Table 2 indicate satisfactory reproducibility in the light of the experimental difficulties.

C. Oxidation Properties

One of the most noteworthy properties of CoO(II) , which had been observed^{25,26} prior to our work, is the rapid absorption of oxygen by the porous CoO(II) lattice. We observed the effect in a direct gravimetric measurement of the weight as a function of the time of exposure to air, and the effect was further verified by observing the transformation of the CoO(II) Mössbauer pattern after exposure to air.

The time dependence of the reaction

as determined by weights is shown in Fig. 6.

The Mössbauer spectra before and after oxygen absorption are shown in Fig. 6. For comparison we show how vacancy-free CoO(I) is completely unaffected after two months' exposure to air. The Mössbauer spectrum of oxygen-saturated CoO(II) has a double line different from that of CoO(II), while the x-ray powder pattern of oxygen-saturated CoO(II) shown in Fig. 7 is in fact nearly the same as that of CoO(II). Also, at low temperatures (77°K) it was observed that the 6 finger hyperfine pattern of CoO(II) disappeared after oxygen saturation at room temperature, becoming a simple quadrupole doublet after sufficient oxygen absorption. The invariance of the x-ray pattern under oxygen absorption was already observed by chemists²⁵. It suggests that the oxygen which diffuses into the CoO(II) lattice fills the anion vacancies of this porous lattice. This additional interstitial oxygen in CoO(II) destroys the internal magnetic field at the Fe⁵⁷ nucleus, but, as expected has slight effect on the x-ray powder pattern. A detailed discussion of our x-ray studies on cobaltous oxide will be given later.

D. Thermal Hysteresis

It would be reasonable to expect a highly vacated structure such as CoO(II) to be a metastable state, which would transform to stable CoO(I) when sufficient thermal energy is supplied. In fact, CoO(II)

Fig. 6

Oxidation properties of CoO(I) and CoO(II) . a) oxygen absorption of CoO(II) as a function of time, as determined by increasing weight. For $\text{CoO(II)} \cdot n\text{O}_2$, n is shown as the ordinate. b), c) Mössbauer spectra at 26°C of CoO(II) before and after exposure to oxygen. d), e) Mössbauer spectra at 26°C of CoO(I) before and after exposure to air for 2 months.

Fig. 6

Fig. 7

X-ray diffraction patterns of CoO(II) before a) and after b) exposure to air. $\text{Mo K}\alpha$ was used for taking the powder patterns.

Fig. 7.

transformed noticeably to CoO(I) above about 300°C with a transformation rate that increased with temperature. The ratio of Fe^{2+} to Fe^{3+} shown in Fig. 8 was determined from the Mössbauer spectra at 24°C after the sample was heated at each temperature for 20 min. in an argon atmosphere.

The conversion of $\text{CoO(II)} \rightarrow \text{CoO(I)}$ on heating in argon was never completed up to about 1000°C for the time period of several hours, and generally left a small number of Schottky defects, giving CoO(I, II) . As we will show in the subsequent discussion, this small number of Schottky defects is not the true equilibrium concentration, but is a non-equilibrium thermodynamic distribution, even though reversible Mössbauer spectra are observed under temperature cycling below 1000°K . Our results indicate that the time required to achieve true thermodynamic equilibrium at these temperatures is large compared to the experimental times. These temperature-dependent Mössbauer results, which give the false appearance of representing a reversible process, were observed previously^{4,11} and agree in essence with our own findings.

E. Pressure and Quenching Experiments

When CoO(I, II) was placed in a mechanical press and an external pressure of approximately 10^4 atmospheres was applied to the sample at room temperature (24°C), it was hoped that CoO(II) might be transformed to CoO(I) . Figs. 9(a) and (b) show the Mössbauer patterns before and after the application of pressure. While the lines broaden there is no clear-cut conversion of II to I, indicating that a pressure of 10^4 atmospheres is insufficient to effect the transformation

Fig. 8

Conversion of CoO(II) to CoO(I) in argon atmosphere. Three examples of Mössbauer spectra taken at room temperature after the sample was heated for 20 min. in an argon atmosphere at temperature a) 24°C , b) 523°C , and c) 750°C , d) the ratio of area of Fe^{2+} to that of Fe^{3+} at room temperature is shown, after heating the sample at each temperature indicated for 20 min. successively.

Fig. 8

Fig. 9

Effects of quenching on the conversion of CoO(II) to CoO(I) .

Mossbauer spectra a) before applying pressure, b) after applying pressure, c) before quenching, and d) after quenching.

Fig. 9

at 24°C. We did not have the facilities to test whether the transformation could be achieved at higher pressure even at room temperature. A variation of the pressure experiment was done by quenching a specimen of CoO(I, II) from 600°C to 0°C and then to 77°K. This experiment was performed in a copper tube filled with an inert atmosphere to ensure rapid cooling in a chemically inactive environment. Although such an experiment lacks sufficient control to permit an accurate assessment of the pressures and stresses placed on the powder specimen, they were found to be large enough to cause the porous form II to transform to the "vacancy-free" pure form I. The Mössbauer patterns giving these results are also shown in Figs. 9(c) and (d), where a sizable fraction of the Fe³⁺ room temperature line is seen to convert to the Fe²⁺ line.

V. $\ddot{\text{M}}\ddot{\text{O}}\text{SSBAUER SPECTRA}$

A. $\ddot{\text{M}}\ddot{\text{O}}\text{ssbauer Spectra}$

In Fig. 10 $\ddot{\text{M}}\ddot{\text{O}}\text{ssbauer}$ spectra of CoO(I) are shown as a function of temperature. Above 288°K the spectra are single lines, but below 288°K they split because of a magnetic hyperfine interaction. The single lines observed above 288°K represent paramagnetic states above the Néel temperature, and the hyperfine patterns below 288°K correspond to the antiferromagnetic state. The apparent Néel temperature in our experiment is then 288°K , three degrees less than that reported by Bizette and LaBlanchetais^{15,16}. This three-degree discrepancy is outside of our experimental errors and probably reflects the limited accuracy of the earlier techniques^{15,16}.

The isomer shift of CoO(I) at 26°C relative to $\text{Na}_4\text{Fe(CN)}_6 \cdot 10\text{H}_2\text{O}$ absorbers is -1.12 mm/sec. From a comparison with the systematics of the isomer shift^{27,28} the $\ddot{\text{M}}\ddot{\text{O}}\text{ssbauer}$ lines from CoO(I) correspond to the divalent compounds. The magnetic hyperfine field at 0°K of about 120 kG also corresponds to the divalent charge state²⁸. The divalent charge state of Fe^{57} in CoO(I) established by the isomer shifts and the magnitude of the magnetic hyperfine field is consistent with our model that CoO(I) has a perfect NaCl structure with essentially no vacancies.

Fig. 10

Mössbauer spectra for CoO(I) as a function of temperature. A
0.75 mg/cm² Na₄Fe(CN)₆ · 10 H₂O absorber was used.

Fig. 10

Mössbauer spectra of CoO(II) over a wide range of temperatures are shown in Fig. 11. Above 270°K the spectra are single lines, but below 270°K they split into the 6 finger patterns in addition to a very broad line with unresolvable structure, whose line width becomes broader with decreasing temperature, and whose depth approaches zero at 77°K . This differed from the magnetic hyperfine patterns of CoO(I) which showed a well defined transition from a six-finger pattern to a single line at 288°K .

As the temperature approached the transition temperature of about 270°K , the broad unresolved line in the Mössbauer spectra of CoO(II) grew and gradually became a single line with the disappearance of the six-finger pattern (Fig. 11). Because the broad unresolved line was superimposed on the observed hyperfine pattern, it was difficult to measure the Néel temperature accurately. A Néel temperature of about 270°K was determined from the maximum intensity value of the single line and should be accurate to within $\pm 10^{\circ}\text{K}$. From the results of x-ray diffraction (see Section VI) it is shown that there is no long-ranged ordering greater than $50\text{\AA}$ for the pure CoO(II) structure, even though short-ranged ordering can still exist. One way of explaining the broad unresolved line is to assume that a fraction of the cobaltous ions in CoO(II) are in disturbed environments from those, which show the resolvable hyperfine pattern. This could result from domain boundaries in form II. The observed x-ray pattern shows that these domains could not be appreciably larger than $50\text{\AA}$. Their influence could also be the reason why the resolvable

Fig. 11

Mössbauer spectra for CoO(II) as a function of temperature. A
1.0 mg/cm² Na₄Fe(CN)₆ · 10 H₂O absorber was used.

Fig. 11

part of the hyperfine pattern showed a substantially broader line width than was observed for CoO(I). The possibility of domains in CoO(II) was not studied in sufficient detail to establish its validity, although no evidence was found which contradicted this hypothesis.

The isomer shift of CoO(II) at 26°C relative to a sodium ferrocyanide absorber is -0.45 mm/sec. This value is a characteristic value for Fe^{3+} as shown in many ferric compounds²⁷. The low temperature magnetic hyperfine field for Fe^{57} in CoO(II) was found to be 553 kG and is characteristic^{29,30} of compounds containing Fe^{3+} . The trivalent charge state of Fe^{57} in CoO(II) can be understood within the framework of our model by assuming that the surrounding negative ion vacancy traps one of the electrons from the iron ion making a defect pair of Fe^{3+} associated with an electron trapped at an anion vacancy.

In Fig. 12 Mössbauer spectra of $\text{CoO(I, II)}_{C,T}$, for T between 77°K and 614°K, are arranged to show the actual time sequence of successive runs starting with (a) and ending with (h). The apparent difference between Figs. 12(b) and (g) is an example of the thermal hysteresis effect discussed earlier. The spectra consists of two kinds of lines, which can be easily identified with Fe^{2+} and Fe^{3+} , respectively, when these are compared with the spectra of CoO(I) and CoO(II) shown in Figs. 10 and 11. These mixed spectra of Fe^{2+} and Fe^{3+} in CoO(I, II) were first observed by Wertheim² and lately by many others^{4-6,11}. Various interpretations for these results have been given, which we already mentioned in the section I, and will

Fig. 12

Mössbauer spectra of CoO(I, II) as a function of temperature.

Fig. 12

discuss in detail in the section IX. While the temperature dependence of the magnetic hyperfine field of Fe^{2+} in CoO(I, II) is the same as that for pure CoO(I) over the full range of temperatures, the magnetic hyperfine field of the Fe^{3+} component of CoO(I, II) is very similar at low temperatures to that of the pure CoO(II) , having a slightly higher Néel temperature than Fe^{3+} in pure CoO(II) , and in fact the same transition temperature as that of CoO(I) . This phenomena can be easily explained by our model which postulates a gradual dispersion of anion vacancies into the CoO(I) structure as the temperature is raised above 200°K . These dispersed anion vacancies cause any surrounding Co^{57} ions to transform to Fe^{3+} after radioactive decay, but the Néel temperature will now correspond to that of CoO(I) instead of CoO(II) . Strong additional evidence for this dispersion of negative ion vacancies will be discussed at the end of this section.

In addition to source experiments Mössbauer absorbers of CoO doped with enriched Fe^{57} were studied. Two absorbers were made; one starting from a chloride and the other starting from a nitrate.

The first absorber was prepared by reducing CoCl_2 doped with FeCl_2 to metallic Co:Fe^{57} in a hydrogen atmosphere above 600°C , and then heating the resulting Co:Fe^{57} in a carbon dioxide atmosphere at 950°C for 5 hours. X-ray diffraction patterns of this absorber were exactly the same as those generally found for CoO(I) . For this absorber experiment Co^{57} in Cu was used as a Mössbauer source. Since the isomer shift of Co^{57} in Cu relative to a sodium ferrocyanide absorber is -0.27 mm/sec, an isomer shift 0.87 mm/sec for this absorber

(Fig. 13(a)) using a Co^{57} in Cu source is equivalent to an isomer shift of -1.14 mm/sec for Fe^{2+} in CoO relative to a sodium ferrocyanide absorber. As this is the identical isomer shift found in the source experiments for Fe^{2+} in CoO(I), we conclude that Fe^{2+} in a CoO(I) absorber is identical to Fe^{2+} resulting from the decay of Co^{57} in CoO(I).

The second absorber was prepared by heating a nitrate at 990°C in an oxygen atmosphere for one hour and in a nitrogen atmosphere for three hours. X-ray diffraction patterns of this absorber were again of the same type as a cobaltous oxide. The Mössbauer spectra for this absorber, however, showed two lines which corresponded to Co^{57} - doped Co_3O_4 (Fig. 13(b)).

Triftshäuser and Craig^{11,14} also prepared two absorbers; one starting from a chloride and the other starting from a nitrate. Although their resonances showed a small percentage effect, because natural iron was used, they claimed that their observed spectra were essentially identical to those obtained using the CoO source. We made two more absorbers, in addition to the above mentioned ones, using enriched Fe^{57} instead of natural Fe, and following the identical recipes as those of Triftshäuser and Craig¹⁴, but obtained the same spectra as Fig. 13(b). The only technique which was found to permit the substitutional implantation of Fe^{3+} in CoO(II) was that resulting from the radioactive decay from a cobalt parent. It was therefore only possible to observe this resonance in source experiments.

Fig. 13

Mössbauer spectra at 26°C for the Fe^{57} -doped cobaltous oxide absorbers. Co^{57} in Cu was used as the source. a) prepared from a chloride b) prepared from a nitrate. Two arrows show the line positions corresponding to Fe^{2+} and Fe^{3+} in CoO(I, II) .

Fig. 13

B. Temperature Dependence of Recoil Free Fraction

Mössbauer recoil free fraction, or f-factor, is proportional to the area under the Mössbauer absorption pattern, and can be expected to decrease as source temperature is increased. This is true for both pure CoO(I) and pure CoO(II) except for possible increases in f near the Néel temperatures (Figs. 14(a) and (e)). Considering the experimental errors, it is doubtful that the sudden increases shown in the f-factors at the Néel points are real, but if they do exist, then they may be connected with a fundamental property associated with the transition from the antiferromagnetic state to the paramagnetic state. On the other hand, the general decreasing tendency of f(T) does not hold for a material such as CoO(I, II)_{C,T}, because of the dispersion of anion vacancies at higher temperatures. This dispersion substantially increases the probability that any given Co⁵⁷ ion will have an adjoining negative ion vacancy, which results in the formation of Fe³⁺ following the radioactive decay of Co⁵⁷. This interplay between CoO(I) and CoO(II) at higher temperatures can, and in fact does, cause the area under the Fe³⁺ absorption curve to increase as the temperature is raised.

In the simple Debye model of a monatomic lattice the recoil free fraction can be written as

$$f \approx \exp\left[-\frac{3}{2} \frac{R}{k\theta_M} \left(1 + \frac{2\pi^2}{3\theta_M^2} T^2\right)\right], \quad (T < \theta_M),$$

where R is the recoil energy, θ_M is the Mössbauer characteristic temperature, and k is Boltzmann's constant. Since the area under

Fig. 14

Temperature dependence of $\ln A$, which is proportional to $\ln f$,
 for Fe^{2+} and Fe^{3+} in cobaltous oxide. a) pure CoO(I)
 b) $\text{CoO(I, II)}_{9\%,T}$ c) $\text{CoO(I, II)}_{11\%,T}$ d) $\text{CoO(I, II)}_{21\%,T}$ e) pure
 CoO(II) , where % represents CoO(II) concentration at 0°K .

Fig. 14

the Mössbauer absorption spectrum is proportional to f , the natural logarithm of the area can be written as:

$$\ln A = a + b(T)T^2$$

where a is a constant, and

$$b(T) \approx - \frac{R\pi^2}{3k\theta_M}, \text{ for } T < \theta_M.$$

Even though these formulas only apply to a monatomic lattice with a Debye frequency spectrum, they are commonly used with more complex lattices, where it is understood that the effective θ_M determined may have little relation to the Debye temperature obtained from specific heat measurements. In Fig. 14 $\ln A$ vs. T^2 for Fe^{2+} and Fe^{3+} in cobaltous oxide are shown with the total area under the entire Mössbauer spectrum adjusted to the same value in the very low temperature limit, i.e., $T \ll \theta_M$. Fig. 14(a) represents pure CoO(I) , which gives an effective Mössbauer characteristic temperature of 510°K from the above equation. CoO(II) has an effective characteristic temperature of only 320°K , however, which is much lower than that of CoO(I) .

This much lower value of θ_M for CoO(II) is in complete accord with our model for form II. The removal of half of the lattice ions means that a cobalt ion in form II has only half as many covalent bonds as a cobalt ion in form I, and so form II nuclei are expected to be less tightly bound. The large difference in effective

Mössbauer characteristic temperature is in the right direction and of the correct magnitude required by our model.

In Figs. 14(b), (c), (d), the intermediate cases between the above two limits, are shown, with the relative percentages of areas under the Fe^{3+} absorption spectra compared with the total absorption areas at 0°K. It might at first seem surprising that the areas of Fe^{3+} increase with increasing temperature, while those of Fe^{2+} decrease more rapidly than that of pure CoO(I) . This tendency for the Fe^{3+} areas to increase with increasing temperature was also observed by Bhide and Shenoy⁴, who attributed this increasing intensity of Fe^{3+} to a reversible increase in the relaxation time of Fe^{3+} with increasing temperature. Later, Triftshäuser and Craig^{11,14} interpreted this increase in Fe^{3+} as a reversible oxidation, which caused an increase of cation vacancies. We found an irreversible process, however, which is in contradiction to both the reversible increase in electronic relaxation time model, and the reversible oxidation model. In Fig. 12 Mössbauer spectra for CoO(I, II) , are arranged in the order of an actual thermal cycle, starting from (a) and ending with (h). The intensity of the Fe^{3+} Mössbauer line became larger as the temperature increased from 296°K, and practically none of the Fe^{2+} line remained at 537°K. When the temperature reached 614°K, however, a large fraction of the cobalt environments producing Fe^{3+} converted irreversibly to Fe^{2+} environments. After this irreversible conversion the Mössbauer spectra were reversible under temperature cycling for a time period comparable to the experimental times. Our observation that Fe^{3+} at 614°K converted to Fe^{2+} , as shown in Fig. 12, is

not only in contradiction to the idea of a reversible increase of electronic relaxation time for Fe^{3+} , proposed by Bhide and Shenoy, but also is not in accord with the assertion of Triftshäuser and Craig^{11,14} that oxidation increases with increasing temperature. According to our model, however, CoO(I, II) consists of CoO(I) and CoO(II) at 0°K , with CoO(II) consisting of clusters formed by the precipitation of Schottky defects. When the temperature is raised sufficiently ($\sim 200^\circ\text{K}$), our results indicate that the anion vacancies begin to move out of the precipitated vacancy clusters of CoO(II) . Dispersing the anion vacancies increases the probability of forming Fe^{3+} , as any given Co^{57} ion will now have approximately a five-fold greater chance of adjoining an anion vacancy. This dispersion of anion vacancies is supported by the rapid absorption of oxygen by CoO(II) at room temperature described earlier, which demonstrates the mobility of the anion vacancies at these temperatures. As temperature increases the fraction of dissociated anion vacancies increases thereby enhancing the Fe^{3+} Mössbauer pattern while decreasing the Fe^{2+} component, until the temperature reaches a critical temperature of about 600°K at which point large clusters of CoO(II) irreversibly collapse to give CoO(I) , leaving only small clusters of CoO(II) behind. The irreversible conversion of large clusters of CoO(II) to CoO(I) was demonstrated for pure CoO(II) in Section IV D, but the small clusters of CoO(II) left behind apparently could not be eliminated by heating up to 1000°C , for typical experimental time periods. Even though these small clusters of CoO(II) give a reversible Mössbauer spectrum under temperature cycling up to 1000°K , they do

not represent a true thermodynamic equilibrium concentration, because the Mössbauer spectrum of the pure CoO(I) is also reversible under temperature cycling as shown in Fig. 14(a). What the true thermodynamic equilibrium concentration is, was not determined because of the size of the relaxation times at the temperatures accessible in our experiment. It is speculated, however, that pure CoO(I) is very close to that of the true thermodynamic equilibrium concentration, of defects, because alkali halides have very small equilibrium concentration of Schottky defects at comparable temperatures. The apparent invariance of Schottky defect concentration below 1000°C is explained by a long relaxation time for reaching thermodynamic equilibrium, and the above-mentioned reversibility of Mössbauer spectra under temperature cycling also can be understood on this basis. Our results indicate that progressively more anion vacancies are disassociated from cation vacancies with increasing temperatures and are dispersed into the CoO(I) structure, thereby increasing the Fe^{3+} Mössbauer line intensity, and when the temperature decreases the dispersed anion vacancies are attracted toward the immobile cation vacancies by Coulomb attraction, giving the apparently reversible Mössbauer spectra.

We will explain the thermal cycle drawn in Fig. 12 using our model and Fig. 14. We will start with the 296°K points along curves 14(c). As the temperature increases the Fe^{2+} and Fe^{3+} spectra follow curves 14(c) until the critical temperature of about 600°K is reached, and then an irreversible transformation occurs which corresponds to a vertical transformation from Figs. 14(c) to 14(b). Temperature cycling below 1000°K does not cause any further transformation,

although as we stated earlier this does not necessarily represent the true thermodynamic equilibrium at these temperatures. It should be noted that the Fe^{3+} part of the curve 14(c) at higher temperatures is even greater than that of pure CoO(II) , as is shown in Fig. 14(e), and is comparable with 14(a) for pure CoO(I) . This phenomenon strongly supports our model, because the Fe^{3+} Mössbauer line of CoO(I, II) at higher temperatures results from the disassociated anion vacancies diffused into CoO(I) , and consequently would be expected to approximately follow the recoil-free fraction curve of CoO(I) instead of pure CoO(II) . A similar phenomenon is found with respect to the Neel temperature. For T_N is 288°K for both Fe^{2+} and Fe^{3+} in $\text{CoO(I, II)}_{C,T}$, having only small clusters of form II ($C < 20\%$), even though the Neel temperature of pure CoO(II) is slightly lower ($\sim 18^\circ\text{K}$) than that of pure CoO(I) . This effect is also explained by our model, i.e., the Fe^{3+} in $\text{CoO(I, II)}_{C,T \approx 300^\circ\text{K}}$ is associated with anion vacancies dispersed into CoO(I) , and therefore is expected to have the Neel temperature of the host material, CoO(I) .

VI. X-RAY PATTERNS

The x-ray diffraction technique has been used for the determination of crystal structures for many years. For a perfect crystal structure with complete translational symmetry the line positions and relative intensities of the diffraction peaks are unique^{31,32}. This is not necessarily true for a structure having many Schottky defects like CoO(II), which gives the same line positions and relative intensities as is found for perfect CoO(I).

The experimental x-ray patterns of CoO(I) and CoO(II) are shown in Fig. 15. From Fig. 15 the experimental line positions and relative intensities for CoO(I) and CoO(II) were calculated and listed in columns 1, 4, and 5 of Table 3. It is clearly seen that the line positions and relative intensities are the same for both CoO(I) and CoO(II) even though the line widths are much broader for form II than for form I.

CoO(I) has the perfect NaCl structure, having 4 cobalt atoms and 4 oxygen atoms at the following coordinates in the unit cell.

$$\begin{array}{ll} \text{Co} & (000), (0\frac{1}{2}\frac{1}{2}), (\frac{1}{2}0\frac{1}{2}), (\frac{1}{2}\frac{1}{2}0) \\ \text{O} & (\frac{1}{2}00), (0\frac{1}{2}0), (00\frac{1}{2}), (\frac{1}{2}\frac{1}{2}\frac{1}{2}) \end{array}$$

Pure CoO(II) has the NaCl structure with half of its cobalt sites and half of its oxygen sites vacant in such a way that each corresponding

Fig. 15

X-ray diffraction patterns of CoO(I) and CoO(II) using Mo $K\alpha_1$ and $K\alpha_2$ x-ray, which was responsible for double peaks at large scattering angles.

Fig. 15

CoO(I) unit cell has two Co sites and two O sites vacant. Since there is no known preferable choice for any particular combination of the two vacant Co and O sites, we have 36 different possible combinations. In order to explain the experimental data it is necessary to assume that there is no long-ranged ordering greater than $50\text{\AA}$, because, calculations show that, some additional lines in addition to the normal lines shown in Fig. 15 would result.

The relative intensities of the x-ray diffraction peaks for a powder sample are proportional to³²

$$I = n \frac{1 + \cos^2 2\theta}{\sin 2\theta \sin \theta} |F_{hkl}|^2,$$

where $F_{hkl} = \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$

h, k, l = Miller indices of a diffraction plane

f_j = atomic scattering factor of j th atom

x_j, y_j, z_j = coordinates of j th atom.

n = number of equivalent planes

θ = diffraction angle.

Using Mo $K\alpha$ x-ray of wavelength $0.7107\text{\AA}$ and the values of f_j from International Tables of Crystallography³³, we calculated the relative intensities of the diffraction lines for CoO(I) and CoO(II). The results gave identical line positions and relative intensities for both CoO(I) and CoO(II) (see column 1 and 2 in Table 3). The calculations were carried out by a 7094 computer, and for the calculation of line positions and intensities of CoO(II) a microcrystal $12 \times 12 \times 12$ times the unit cell specified above for CoO(I) was used, with the condition

Table 3. Relative line intensities of x-ray patterns of cobaltous oxide.

Theoretical Values			Experimental Values	
2θ	CoO(I) and CoO(II)	25% cation vacancies	CoO(I)	CoO(II)
16.6°	71	49	70	73
19.2°	100	100	100	100
27.3°	64	63	63	66
32.1°	35	26	32	38
33.6°	21	20	22	18
39°	9	9	9	7
42.7°	14	11	14	10
43.8°	24	23	22	18

that no long-ranged ordering be permitted between vacancies in the microcrystal.

It is clearly seen that the experimental values in columns 4 and 5 are in good agreement with the theoretical values in column 2 based on our model. It is noticeable in Fig. 15 that the linewidths of CoO(II) are substantially broader than those of CoO(I). This can be understood if our sample consisted of ordered domains of sizes not greater than about $50\text{\AA}$. The disorientation between two adjoining grains (domains) renders their scattering completely incoherent, so that they act as if they were separated. Since the domains are small in size, the x-ray diffraction lines are broadened by the size effect³⁴. Failure to observe any additional x-ray lines for form II indicates that any short-ranged ordering within a domain cannot be identical to that in nearby domains. This is plausible since there are 36 different ways of arranging 2 Schottky defects in the perfect CoO(I) unit cell, specified above.

If each domain has different short-ranged ordering, Fe^{57} ions in different domains will have different arrangements of nearest neighbors, and different charge asymmetries will produce different electric field gradients, each of which generally cause some splitting due to interaction with the nuclear quadrupole moment. The domain picture then can explain both the broadened x-ray lines and Mössbauer spectra for CoO(II). It should also be noted that asymmetries in the charge distributions caused by the trapped electrons at different anion vacancies which adjoin the Fe^{3+} ions, will be another source of

electric field gradient, which also can account for the broadening of the hyperfine lines observed in CoO(II) .

It might be conjectured that the TC model would be in less severe contradiction with our experimental results, such as the measured low density, if the density of cation vacancies were allowed to be at a large fraction of the lattice sites. This, however, would not only be in contradiction with our gravimetric measurements of stoichiometry for each form of cobaltous oxide, but it would result in a x-ray powder pattern giving a different intensity distribution than that actually observed. To demonstrate this we assumed a 25% cation vacancy density randomly distributed in an otherwise perfect CoO(I) lattice. The calculated relative intensity distribution is shown in Table 3, and it is in obvious disagreement with the experimental results. Therefore, a cation vacancy model, either of the low concentration type suggested by Triftshäuser and Craig or of the high concentration type, is not consistent with our experimental results.

VII. THEORY

A. Hamiltonian for the Combined Magnetic Hyperfine and Electric Quadrupole Interaction.

Recently, Mössbauer spectra have been used widely for investigations of the magnetic hyperfine field and quadrupole interaction at the site of a nucleus. The Hamiltonian for the $I=3/2$ first excited state of Fe^{57} may be written as³⁵:

$$\mathcal{H}_e = g_1 \mu_N \vec{I} \cdot \vec{H} + \frac{e^2 q Q}{2I(2I-1)} [3I_z^2 - \vec{I}^2 + \eta(I_x^2 - I_y^2)],$$

where $x'y'z'$ represent the principal axes of the electric field gradient tensor, which are chosen so that $|V_{z'z'}| \geq |V_{y'y'}| \geq |V_{x'x'}|$, and where $\vec{H}$ is the internal magnetic field at the nucleus. The electric field gradient along z' is eq , and η is the asymmetry parameter in the $x'y'z'$ frame of reference. g_1 is the absolute value of the g -factor for the first excited state of Fe^{57} , and μ_N is the nuclear magneton. Q is the nuclear quadrupole moment of the first excited state of Fe^{57} multiplied by the Sternheimer factor $(1-R)$.

If $\vec{H}$ has a polar angle θ and an azimuthal angle of ϕ with respect to the $x'y'z'$ -axes, and we take the quantization z -axis along $\vec{H}$

and the x,y-axes as shown in Fig. 16, $\mathcal{K}_e$ will become, on transforming from $x'y'z'$ to xyz,

$$\begin{aligned}
 \mathcal{K}_e = & I_z + \frac{P}{8} (I_+ I_- + I_- I_+) (3 - \eta \cos 2\phi) \sin^2 \theta - \frac{P}{2} I^2 + \frac{P}{2} I_z^2 \\
 & \cdot (3 \cos^2 \theta + \eta \sin^2 \theta \cos 2\phi) + \frac{P}{4} (I_+ I_z + I_z I_+) [-3 \sin \theta \cos \theta \\
 & + \eta \sin \theta (\cos \theta \cos 2\phi + i \sin 2\phi)] + \frac{P}{8} I_+^2 [3 \sin^2 \theta + \eta \cos 2\phi \\
 & \cdot (1 + \cos^2 \theta) + 2i\eta \cos \theta \sin 2\phi] + \frac{P}{4} (I_- I_z + I_z I_-) [-3 \sin \theta \\
 & \cdot \cos \theta + \eta \sin \theta (\cos \theta \cos 2\phi - i \sin 2\phi)] + \frac{P}{8} I_-^2 [3 \sin^2 \theta + \eta \cos 2\phi \\
 & \cdot (1 + \cos^2 \theta) - 2i\eta \cos \theta \sin 2\phi],
 \end{aligned}$$

where energies are expressed in units of $g_1 \mu_N H$, and $P \equiv e^2 q Q / 6 g_1 \mu_N H$.

In the above transformation the following relation between the primed and unprimed components of $\vec{I}$ is used:

$$\begin{pmatrix} I_x' \\ I_y' \\ I_z' \end{pmatrix} = \begin{pmatrix} \cos \theta \cos \phi & -\sin \phi & \sin \theta \cos \phi \\ \cos \theta \sin \phi & \cos \phi & \sin \theta \sin \phi \\ -\sin \theta & 0 & \cos \theta \end{pmatrix} \begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix}.$$

Fig. 16. Direction of $\vec{H}$ with respect to the principal axes $x' y' z'$ of the electric field gradient tensor. In transforming from the $x' y' z'$ frame to the $x y z$ frame a rotation about z' of angle ϕ is followed by a rotation of angle θ about the y axis.

The Hamiltonian matrix for the first excited state of Fe^{57} is

$M_I \backslash M_I'$	3/2	1/2	-1/2	-3/2
3/2	$\mathcal{H}_{11}$	$\mathcal{H}_{21}^*$	$\mathcal{H}_{31}^*$	0
1/2	$\mathcal{H}_{21}$	$\mathcal{H}_{22}$	0	$\mathcal{H}_{42}^*$
-1/2	$\mathcal{H}_{31}$	0	$\mathcal{H}_{33}$	$\mathcal{H}_{43}^*$
-3/2	0	$\mathcal{H}_{42}$	$\mathcal{H}_{43}$	$\mathcal{H}_{44}$

where asterisks stand for complex conjugates, and

$$\mathcal{H}_{11} = 3/2 + (9/8)P (3 \cos^2 \theta + \eta \sin^2 \theta \cos 2\phi) - (15/8)P + (3/8)P \\ \cdot (3 - \eta \cos 2\phi) \sin^2 \theta$$

$$\mathcal{H}_{22} = 1/2 + (7/8)P (3 - \eta \cos 2\phi) \sin^2 \theta + (1/8)P (3 \cos^2 \theta + \eta \sin^2 \theta \cos 2\phi) \\ - (15/8)P$$

$$\mathcal{H}_{33} = \mathcal{H}_{22} - 1$$

$$\mathcal{H}_{44} = \mathcal{H}_{11} - 3$$

$$\mathcal{H}_{21} = -\mathcal{H}_{43} = \frac{\sqrt{3}}{2}P [-3 \sin \theta \cos \theta + \eta \sin \theta (\cos \theta \cos 2\phi - i \sin 2\phi)]$$

$$\mathcal{H}_{31} = \mathcal{H}_{42} = \frac{\sqrt{3}}{4}P [3 \sin^2 \theta + \eta \cos 2\phi (1 + \cos^2 \theta) - 2i\eta \cos \theta \sin 2\phi]$$

By diagonalizing the 4×4 matrix, one can obtain the energy eigenvalues T_n ($n=1,2,3,4$) of the first excited state of Fe^{57} , and the corresponding eigenvectors

$$|\phi_n\rangle = a_{1n}|3/2, 3/2\rangle + a_{2n}|3/2, 1/2\rangle + a_{3n}|3/2, -1/2\rangle + a_{4n}|3/2, -3/2\rangle.$$

On the other hand, since the ground state ($I=1/2$) has no quadrupole moment the perturbed energies and their corresponding eigenvectors in the xyz frame will be

$$\frac{g_0 \mu_N H}{2} |1/2, -1/2\rangle,$$

and

$$\frac{-g_0 \mu_N H}{2} |1/2, 1/2\rangle,$$

where g_0 is the magnitude of the g-factor of the ground state of Fe^{57} nuclei.

Since the gamma ray transitions between the first excited state and the ground state of Fe^{57} are of pure M1 type³⁶, the transition probabilities between the four non-degenerate levels corresponding to the excited state and the two levels corresponding to the ground state (Fig. 17) can be calculated as follows: The transition probability of emitting a γ -ray in the direction of $\vec{k}(\theta_k, \phi_k)$ for an M1 type transition of polarization $M(+1$ or $-1)$ is proportional to³⁷

$$T_{if}^M(\theta_k, \phi_k) = \left| \sum_{M'=0, \pm 1} \mathcal{D}_{M'M}^{(1)*}(\theta_k, \phi_k, 0) \right|^2$$

$$= \left| \langle \psi_i | \sum_{i=1}^A (g_{s_i} s_i^{M'} + g_{l_i} l_i^{M'}) | \psi_f \rangle \right|^2,$$

where (θ_k, ϕ_k) are the polar and azimuthal angles of $\vec{k}$ (the direction of γ -ray emission), and $\mathcal{D}^{(\ell)}(\theta_k, \phi_k, \chi_k)$ is the ℓ -th irreducible representation of the rotation group and θ_k, ϕ_k, χ_k are the Euler

Fig. 17. Energy level scheme for the first excited states and the ground states of an Fe^{57} nucleus.

angles of the coordinate transformation from the xyz-system to a new system, which, in the present case, is such that the new z-axis is along $\vec{k}$ and χ_k is taken to be zero for convenience.

$\mathcal{D}_{M'M}^{(1)}(\theta_k, \phi_k, 0)$ satisfy the orthogonality relation³⁸,

$$\int \mathcal{D}_{M_1 M_1'}^{(1)*}(\theta_k, \phi_k, 0) \mathcal{D}_{M_2 M_2'}^{(1)}(\theta_k, \phi_k, 0) \sin \theta_k d\theta_k d\phi_k = \frac{4\pi}{3} \delta_{M_1 M_2} \delta_{M_1' M_2'}.$$

$$g_{l_i} = \begin{cases} +1 & \text{for protons} \\ 0 & \text{for neutrons} \end{cases},$$

g_{s_i} = intrinsic g-factor of the i-th nucleon, $s_i^{M'}$, $l_i^{M'} = M'$ components of the spin and orbital angular momenta of i-th nucleon ($M' = 0, \pm 1$), and ψ_i, ψ_f = initial and final nuclear wave functions. The intensity of the Mössbauer line, which corresponds to the transition $|\phi_n\rangle \rightarrow |1/2, m\rangle$ ($m = 1/2$ or $-1/2$), is proportional to

$$\begin{aligned} & \sum_{M=\pm 1} \left| \sum_{M'} \mathcal{D}_{M'M}^{(1)*}(\theta_k, \phi_k, 0) a_{1n}^* \langle 3/2, 3/2 | \eta_1^{M'} | 1/2, m \rangle \right. \\ & + \sum_{M'} \mathcal{D}_{M'M}^{(1)*}(\theta_k, \phi_k, 0) a_{2n}^* \langle 3/2, 1/2 | \eta_1^{M'} | 1/2, m \rangle \\ & + \sum_{M'} \mathcal{D}_{M'M}^{(1)*}(\theta_k, \phi_k, 0) a_{3n}^* \langle 3/2, -1/2 | \eta_1^{M'} | 1/2, m \rangle \\ & \left. + \sum_{M'} \mathcal{D}_{M'M}^{(1)*}(\theta_k, \phi_k, 0) a_{4n}^* \langle 3/2, -3/2 | \eta_1^{M'} | 1/2, m \rangle \right|^2, \end{aligned}$$

where $\eta_1^{M'} = g_{s_i} s_i^{M'} + g_{l_i} l_i^{M'}$. For a polarization experiment, the summation over M should be dropped. By the Wigner-Eckart theorem each matrix element in the above expression is proportional to a

Clebsch-Gordan coefficient. Therefore the relative intensities of the eight Mössbauer lines for a powder sample having an isotropic Debye-Waller factor can be easily found by integrating the above expression over θ_k and ϕ_k , and using the orthogonality relation on $\mathcal{D}_{M'M}^{(1)}(\theta_k, \phi_k, 0)$. If there is an angular dependence to the recoil free fraction, in the single crystal case, then the intensity analysis given is not rigorously correct. Nevertheless, it should be approximately true in all cases except those involving exceptionally large anisotropies in the directional dependence of the binding. The results are shown in Table 4 along with the corresponding energy of each allowed transition. It should be noted that the expressions for the relative intensities are much simpler than those reported elsewhere^{39,40}, and in fact could have been written immediately by noting that the contributions of various a_{mn} components are always either 1, 2, or 3 depending on the change of magnetic quantum number relating to that component. By fitting the eight lines having the relative line positions and the relative intensities in Table 4 to Mössbauer data, one can find the optimum values of θ , ϕ , η , and P . The fifth parameter H is simply calculated from the proportionality constant of relative line positions (See column 2 in Table 4). We can obtain $e^2 q Q / 2$ from the relation

$$\frac{e^2 q Q}{2} = 3 P g_1 \mu_N H.$$

Recently, Kündig³⁹ and Hoy and Chandra⁴⁰ treated the same problem discussed here, but they took the quantization axis along a principal

Table 4. The energies and relative intensities for Fe^{57} Mössbauer spectra under the combined magnetic hyperfine and electric quadrupole interaction.

Number	Energy	Relative Intensity
1	$(g_1 T_1 + \frac{g_o}{2}) \mu_N H$	$3 a_{11} ^2 + 2 a_{21} ^2 + a_{31} ^2$
2	$(g_1 T_2 + \frac{g_o}{2}) \mu_N H$	$3 a_{12} ^2 + 2 a_{22} ^2 + a_{32} ^2$
3	$(g_1 T_1 - \frac{g_o}{2}) \mu_N H$	$ a_{21} ^2 + 2 a_{31} ^2 + 3 a_{41} ^2$
4	$(g_1 T_3 + \frac{g_o}{2}) \mu_N H$	$3 a_{13} ^2 + 2 a_{23} ^2 + a_{33} ^2$
5	$(g_1 T_2 - \frac{g_o}{2}) \mu_N H$	$ a_{22} ^2 + 2 a_{32} ^2 + 3 a_{42} ^2$
6	$(g_1 T_4 + \frac{g_o}{2}) \mu_N H$	$3 a_{14} ^2 + 2 a_{24} ^2 + a_{34} ^2$
7	$(g_1 T_3 - \frac{g_o}{2}) \mu_N H$	$ a_{23} ^2 + 2 a_{33} ^2 + 3 a_{43} ^2$
8	$(g_1 T_4 - \frac{g_o}{2}) \mu_N H$	$ a_{24} ^2 + 2 a_{34} ^2 + 3 a_{44} ^2$

axis of the electric field gradient. Their method requires the diagonalization of both 4×4 matrix for the excited state and a 2×2 matrix for the ground state, and gives a complicated expression for the relative intensities of the hyperfine lines. Our method, however, requires only the diagonalization of one 4×4 matrix which has 4 zero elements, and gives much simpler expressions for the Mössbauer line intensities (See Table 4). For the most common cases ($\phi = 0$ or $\pm 90^\circ$) our 4×4 matrix is real, which simplifies the calculation. S.V. Karyagin⁴¹ has given a treatment of this problem from the same approach as used here, although his analysis is not as immediately applicable to computer techniques as the one given above.

B. Crystal Field Theory

The magnetic hyperfine field and the electric field gradient at a nucleus result from the surrounding electrons and ions. Consequently, in order to understand the origins and temperature dependences of the magnetic hyperfine field and the electric field gradient, it is necessary to know the splitting of the electronic levels caused by the crystal field, spin-orbit coupling, and the exchange interaction. Since the interactions affecting electronic levels are different from material to material, we will restrict our argument to CoO(I) . After obtaining the splittings for the electronic levels of Fe^{57} ions in CoO(I) , by diagonalizing the perturbation matrix, we will calculate the contributions of each split level to the magnetic hyperfine field and the electric field gradient at the Fe^{57} nucleus. The ensemble averages of these contributions at each temperature will

give the temperature dependences of the magnetic hyperfine field and electric field gradient. Finally, we will try to explain the temperature dependences of the magnetic hyperfine field and electric field gradient obtained from our Mössbauer spectra (See Section A) in terms of the results obtained from crystal field theory using the method described above.

According to Hund's rules, a free Fe^{2+} ion is in a $5D$ state, which splits into d_γ and d_ϵ levels under the cubic octahedral field^{42,43} (See Appendix A). Since the d_γ levels are generally about 10^4 cm^{-1} higher than the d_ϵ levels, they do not contribute to the magnetic hyperfine field and electric field gradient at ordinary temperatures, and hence they will be neglected. The following three d_ϵ functions behave like the eigen functions of the angular momentum $l=1$ if we put $\vec{l} = -\vec{L}$ where $\vec{L}$ is proportional to the orbital angular momentum, and $\vec{l}$ can be considered as a pseudoangular momentum^{42,44},

$$\psi_1 = Y_2^{-1},$$

$$\psi_0 = (Y_2^2 - Y_2^{-2}) / \sqrt{2},$$

$$\psi_{-1} = -Y_2^1.$$

When the spin functions χ_j ($j=0, \pm 1, \pm 2$) are included, 15 wave functions $(\psi_i \chi_j, i=0, \pm 1, j=0, \pm 1, \pm 2)$ belong to the d_ϵ level. These 15-fold degenerate states will be split under the following

perturbations^{22,44} (See Appendix A)

$$3C' = \lambda \vec{L} \cdot \vec{S} - 2 \sum_i J_i \vec{S}_i \cdot \vec{S} + \lambda \Delta (3I_z^2 - 2)$$

The first term represents the spin-orbit coupling. The spin-orbit coupling constant λ can be written⁴⁵ approximately as a product of the free ion value λ_0 ($= -103 \text{ cm}^{-1}$ for a free Fe^{2+} ion) and a covalency factor α^2 , which accounts for the decrease due to the covalency effect. The second term represents the Heisenberg exchange interaction between an Fe^{2+} spin $\vec{S}$ and host spin $\vec{S}_i$, and J_i is the exchange interaction constant between $\vec{S}_i$ and $\vec{S}$. The last term corresponds to the tetragonal distortion below the Néel temperature. Δ represents a proportionality constant and is assumed to be proportional to the fractional contraction of the lattice parameter c . As described in detail in the introduction, many models on the spin arrangement in CoO have been suggested, but unfortunately, the detailed composition of most CoO samples used in earlier experiments were unknown. Since the usual methods of preparation of CoO give CoO(I, II), as shown in our preceding paper, samples were not likely to be pure CoO(I), which has a perfect NaCl structure with no vacancies. Therefore, we can not accept without some reservation the results of the neutron diffraction studies of the spin directions in CoO. We will assume the collinear model, however, with the angle θ_0 between the spin direction and $[001]$ taken as an unknown for pure CoO(I). The spin direction of Co^{2+} with respect to the crystal axes is then $[\bar{1}, \bar{1}, \sqrt{2} \cot \theta_0]$. This collinear model is not vital to the analysis,

but it is useful in relating θ_0 from the analysis to the spin orientation, because the spin will be parallel to the molecular field in this case.

In terms of the pseudoangular momentum $\vec{l}$, assuming the validity of the molecular field approximation⁴⁴, we obtain for $\mathcal{H}'$

$$\mathcal{H}' = -\lambda \vec{l} \cdot \vec{S} + \lambda \beta \langle S_i \rangle \vec{M} \cdot \vec{S} + \lambda \Delta (3l_z^2 - 2)$$

where $\vec{M}$ is a unit vector in the molecular-field direction, β is the molecular-field constant, and $\langle S_i \rangle$ is the statistical average of $\vec{S}_i$. In order to obtain the energy levels and their corresponding eigenvectors it is necessary to diagonalize the following 15 x 15 matrix (See Appendix C):

$$\langle \psi_i \chi_j | \mathcal{H}' | \psi_{i'} \chi_{j'} \rangle,$$

where $i, i' = 0, \pm 1$ and $j, j' = 0, \pm 1, \pm 2$. The solution of the secular equation will give the eigenvalues E_n , and the corresponding eigenfunctions can be expressed in the form where

$$\Phi_n = \sum_{m=1}^{15} \psi_m a_{mn},$$

where $\psi_m (m=1, 2, \dots, 15)$ is an abbreviation for the 15 wave functions, $\psi_i \chi_j$.

The effective magnetic field acting on a nucleus in a solid is regarded as the sum of the following contributions⁴⁶ (See Appendix B):

(a) The field produced by the orbital magnetic moment on the parent atom

$$\vec{H}_L = 2\mu_B \langle r^{-3} \rangle \langle \vec{L} \rangle \alpha^2,$$

where μ_B is the Bohr magneton and the expectation values refer to the 3d electron. The vector $\vec{r}$ refers to the vector distance from the nucleus to the 3d electron. $\vec{L}$ is the orbital angular momentum operator divided by $\hbar$.

(b) The field proportional to the spin density at the nucleus is

$$\vec{H}_S = (16\pi/3)\mu_B \langle \sum_i \vec{s}_i \delta(r_i) \rangle = (1/2) H_c \langle \vec{S} \rangle,$$

where H_c is the contact term effective field and has been calculated to be about -550 kG for a free ion⁴⁷. $\vec{s}_i$ is the spin angular momentum of the i -th s electron divided by $\hbar$, and $\vec{S}$ is the net spin/ $\hbar$ for the 3d shell. We assume here that the spin polarization of the s electrons is proportional to the spin of the 3d shell. The proportionality constant H_c is taken as a parameter in our analysis, and was generally found to be slightly smaller than the explicitly calculated free ion value.

(c) The field produced by the dipolar interaction with the spin moment on the parent atom

$$\vec{H}_D = 2\mu_B \langle 3\vec{r}(\vec{S}' \cdot \vec{r})r^{-5} - \vec{S}'r^{-3} \rangle = -(1/2)\mu_B \langle 3\vec{r}(\vec{S} \cdot \vec{r})r^{-5} - \vec{S}r^{-3} \rangle,$$

where $\vec{S}'$ relates to the spin of the one 3d electron outside of the closed subshell with aligned spin, and $\vec{S}$ again relates to the net spin of all electrons in the 3d shell. If one takes

$$\vec{h}_D = [3 \vec{S} \cdot (\vec{r}/r)]\vec{r}/r - \vec{S}$$

$\vec{H}_D$ can be written as

$$\vec{H}_D = -(1/2)\mu_B \langle r^{-3} \rangle \alpha^2 \langle \vec{h}_D \rangle.$$

The total magnetic hyperfine field at the Fe^{57} nucleus is the sum of the above three contributions:

$$\vec{H} = \vec{H}_L + \vec{H}_S + \vec{H}_D$$

Because the nuclear lifetime of the first excited state of Fe^{57} is only 10^{-7} seconds, and the transitions between electronic states can be of order 10^{-8} sec or greater, it is not obvious that time averages and ensemble averages are equivalent, even though they are commonly assumed to be so^{22,45}. We also will assume that transition times between the 15 perturbed levels are sufficiently short as to permit ensemble averages of $\vec{L}$ and $\vec{S}$ for the case of CoO(I) . For

an operator O , the ensemble average can be written as

$$\langle O \rangle = \text{Tr } O\rho,$$

where ρ is the density operator

$$\frac{\exp (-\mathcal{H}'/kT)}{\text{Tr } [\exp (-\mathcal{H}'/kT)]}.$$

Specifically, for a representation in which $\mathcal{H}'$ is diagonal, $\langle O \rangle$ can be written explicitly as

$$\langle O \rangle = \frac{\sum_{n=1}^{15} O_{nn} \exp (-E_n/kT)}{\sum_{n=1}^{15} \exp (-E_n/kT)}.$$

In this representation the following ensemble averages, $\langle \vec{L} \rangle$, $\langle \vec{S} \rangle$, and $\langle \vec{h}_D \rangle$, are easily calculated in accordance with the above prescription (See Appendix C for explicit evaluation of the quantum expectation values). The temperature dependence of the magnetic hyperfine field follows when the above $\langle \vec{L} \rangle$, $\langle \vec{S} \rangle$, and $\langle \vec{h}_D \rangle$ are substituted into the expressions for $\vec{H}_L$, $\vec{H}_S$, and $\vec{H}_D$. For the present case including tetragonal distortion $\vec{H}_L$, $\vec{H}_S$, and $\vec{H}_D$ are in general not parallel to $\vec{M}$.

The most important contribution to the electric field gradient at the Fe^{57} nucleus is due to the aspherical charge distribution of the 3d electrons belonging to the ferrous ion. The other smaller contribution arises from the charge distribution of the neighboring ions in the crystalline lattice, and it is neglected in this paper, because CoO(I) is almost cubic and the lattice contribution to the

electric field gradient does not exceed one percent of that due to the 3d electron if one follows Ingalls' estimation⁴⁵. The electric field gradient tensor due to the 3d electron outside of the half-filled 3d shell can be written as follows at a given temperature,

$$V_{ij} = -e \langle (3x_i x_j - r^2 \delta_{ij}) r^{-5} \rangle = -e \langle r^{-3} \rangle \alpha^2 \langle 3x_i x_j r^{-2} - \delta_{ij} \rangle.$$

Where $x_1 x_2 x_3$ are the xyz coordinates of the 3d electron, and $i, j=1,2,3$. In the last expression $\langle 3x_i x_j r^{-2} - \delta_{ij} \rangle$ is the ensemble average of the expectation values of the bracketed terms. In order to get the principal axes of V_{ij} it is necessary to diagonalize $\|V_{ij}\|$; i.e., $\tilde{V}' = \tilde{B}^{-1} \tilde{V} \tilde{B}$ where $\tilde{B} = \|b_{ij}\|$, $\tilde{V} = \|V_{ij}\|$, $\tilde{V}'$ is a diagonal matrix whose elements are arranged in such a way that

$$|V_{33}'| \geq |V_{22}'| \geq |V_{11}'|.$$

We take the coupling constant for the quadrupole interaction to be

$$(1/2)e^2 q Q = (1/2)e Q V_{33}',$$

where Q is the nuclear quadrupole moment of the first excited state of Fe^{57} multiplied by the Sternheimer factor $(1-R)$, which corrects for the polarization of the ferric-like ($^6S, 3d^5$) core by the electric field gradient due to the 3d electron with opposed spin. The asymmetry factor η is given by

$$\eta = (V_{11}' - V_{22}') / V_{33}'.$$

The polar and azimuthal angles of $\vec{H}$ in the coordinate system of the principal axes of the electric field gradient tensor are

$$\theta = \cos^{-1} (H_x b_{13} + H_y b_{23} + H_z b_{33}) / H,$$

and

$$\phi = \tan^{-1} \frac{H_x b_{12} + H_y b_{22} + H_z b_{32}}{H_x b_{11} + H_y b_{21} + H_z b_{31}},$$

where H_x , H_y , and H_z are the cartesian components of $\vec{H}$.

Using the above formalism, one can find the optimum values of H_c , α^2 , $\langle r^{-3} \rangle$, Q and the spin direction of the host Co^{2+} , such that the derived H , $(1/2)e^2qQ$, η , θ , and ϕ are fitted to those determined from experimental data described in Section A. $\beta \langle S_i \rangle$ and Δ are assumed to be proportional to the sublattice magnetization and lattice distortion, respectively, and the proportionality constants are also determined from the above fitting.

VIII. ANALYSIS OF EXPERIMENTAL DATA

A. CoO(I)

Mössbauer hyperfine spectra below the Néel temperature are shown in Fig. 18. The patterns indicate a pure magnetic hyperfine interaction from 288°K to 243°K, but a contribution from the quadrupole interaction is evident for those resonances shown at $T = 195^\circ\text{K}$ and below. Before trying to fit the eight lines in Table 4 to the data by varying θ , ϕ , η , and P , one may limit θ or ϕ to a few values by a simple symmetry argument. According to x-ray and neutron diffraction experiments the crystal distortion and spin arrangements are symmetrical about the (110) plane. Therefore, we may assume that one of the principal axes of the electric field gradient is perpendicular to the (110) plane, and that the other two principal axes and $\vec{H}$ are in the (110) plane. In this case only limited choices of ϕ or θ are possible; when the principal axis corresponding to the maximum field gradient is in the (110) plane, $\phi = \pm 90^\circ$ or 0° . When the z' axis is perpendicular to the (110) plane, $\theta = 90^\circ$. Using an IBM 7094 computer to fit the eight lines with the relative line positions and relative line intensities in Table 4 to the Mössbauer data of CoO(I) at each temperature, we find ϕ (-90°), H , $\frac{e^2qQ}{2}$, η , and θ as a function of temperature, as shown in Figs. 19 through 22. The data were fitted by assuming the Mössbauer spectra consisted of eight Lorentzian

Fig. 18

Mössbauer spectra of CoO(I) below the Néel point at various temperatures. A 0.75 mg/cm^2 $\text{Na}_4 \text{Fe(CN)}_6 \cdot 10 \text{ H}_2\text{O}$ absorber was used.

Fig. 18

curves, and the sum of the eight Lorentzians are drawn on the data points in Fig. 18, along with a schematic of intensities of its constituent lines. In Fig. 19 the magnetic hyperfine field has a maximum at about 180°K, and then decreases with decreasing temperature. The same tendency was also observed in MnO and NiO by Siegwarth²². The quadrupole interaction, however, increases in magnitude with decreasing temperatures (Fig. 20). η and θ values are fairly constant under temperature variation, namely, about 0.40 ± 0.05 and about $42^\circ \pm 5^\circ$, respectively (Figs. 21 and 22). From Fig. 18 the transition temperature from the hyperfine patterns to a single line pattern is seen to be 288°K, which is three degrees lower than the value measured by Bizette¹⁵ and La Blanchetais¹⁶. This three-degree discrepancy is outside of our experimental errors and probably reflects the limited accuracy of the earlier techniques.

We will try to explain temperature-dependence of H , $\frac{e^2qQ}{2}$, θ , and η in terms of the crystal field theory developed in Section VII B. Using a Brillouin function with $S = 3/2$ as an approximation of $\beta \langle S_i \rangle$ and varying the previously mentioned parameters, we tried to fit the theoretical H , $\frac{e^2qQ}{2}$, θ , and η of the crystal field theory to those obtained from the Mössbauer spectra, and found the following to be the optimum values:

$$\text{Spin direction} = [\bar{1}\bar{1}3]$$

$$H_c = -448 \text{ kG}$$

$$\alpha^2 = 0.69$$

$$\langle r^{-3} \rangle = 4.4 \text{ a.u.}$$

$$Q = 0.21 \text{ b}$$

Fig. 19

Temperature dependence of the magnetic hyperfine field at Fe^{57} nuclei in CoO(I) . The points with error bars are determined from Mössbauer spectra by diagonalizing the magnetic hyperfine and electric quadrupole interaction Hamiltonian matrix (4×4) . The solid curve is determined by the crystal field theory.

Fig. 19

Fig. 20. Temperature-dependence of $\frac{e^2 q Q}{2}$ in CoO(I).

Fig. 21. Temperature-dependence of η in CoO(I) .

Fig. 22. Temperature-dependence of θ in CoO(I) .

The zero-point values of $\beta\langle S_i \rangle$ and Δ were found to be 2.55 and 0.09, respectively. As expected the calculation gave -90° for ϕ at all temperatures. The theoretical curves are drawn in Figs. 19 through 22 (see solid lines) and are in good agreement with the values determined from Mössbauer spectra. The adjusted parameters are in reasonable agreement with currently reported values; $\langle r^{-3} \rangle = 4.4$ a.u. is the same as Okiji and Kanamori's value⁴⁸, $Q = 0.21$ b which contains the Sternheimer factor is the same as Ingall's value⁴⁵. The spin direction $[\bar{1}\bar{1}3]$, which is 25° from the c-axis, is almost the same as van Laar's value of $\theta_0 = 27.4^\circ$. In Fig. 23 the temperature-dependences of the 15 split energy levels are shown. Below about 100°K the energy levels and their eigenfunctions are almost independent of temperature, and therefore, the temperature dependence of the magnetic hyperfine field can be easily understood from the statistical population of these levels. In Table 5 the x and z components of $\langle \Phi_n | \vec{L} | \Phi_n \rangle$ and $\langle \Phi_n | \vec{S} | \Phi_n \rangle$ ($n = 1, 2, \dots, 15$) are shown along with their corresponding energy levels (the y components are the same as the x components by symmetry or by direct calculation). Orbital angular momentum in some lower excited states has the opposite sign to that in the ground state, while spin angular momentum in lower excited states has the same sign as that in the ground state (Table 6). Therefore, the orbital angular momentum quenches more rapidly than the spin angular momentum with increasing temperature. The spin angular momentum $\langle \vec{S} \rangle$ and the orbital angular momentum $\langle \vec{L} \rangle$ give the opposite contributions to the magnetic hyperfine field (see the expressions for $\vec{H}_L$ and $\vec{H}_S$ in section VII B). The ground state

Fig. 23

Temperature dependence of the 15 energy levels of Fe^{2+} ion in CoO(I) originating from d_e level. Energies are represented in units of the spin-orbit coupling constant ($|\lambda| = 102.3^\circ\text{K}$).

Fig. 23

Table 5. Eigenenergies due to $\mathcal{H}$, their associated angular momenta, and quadrupole coupling constant below 100°K .

n	E_n ($^\circ\text{K}$)	$\langle L_x \rangle_n$	$\langle L_z \rangle_n$	$\langle S_x \rangle_n$	$\langle S_z \rangle_n$	$\langle \frac{e^2 q Q}{2} \rangle_n$ (mm/sec)
15	720	0.351	0.868	-0.627	-1.792	-1.706
14	615	0.008	0.260	-0.492	-1.622	2.210
13	471	-0.097	-0.316	-0.391	-1.227	0.991
12	290	-0.170	-0.511	-0.179	-0.533	-0.513
11	275	0.215	0.679	-0.369	-1.113	0.670
10	210	-0.107	-0.345	-0.416	-1.244	-0.359
9	93	-0.235	-0.669	0.067	0.234	-0.492
8	-47	-0.020	-0.246	-0.059	-0.221	0.751
7	-103	0.179	0.680	-0.088	-0.244	-0.616
6	-112	-0.280	-0.788	0.316	1.024	-1.116
5	-304	-0.004	-0.180	0.277	0.742	1.799
4	-324	-0.318	-0.891	0.570	1.828	-1.715
3	-447	0.216	0.757	0.232	0.748	-0.950
2	-561	0.016	-0.141	0.606	1.676	2.870
1	-776	0.245	0.843	0.553	1.744	-1.348

contributions to the x, y, and z components are calculated to be

$$\langle \vec{H}_S \rangle_1 = (-135, -135, -426) \text{ kG}$$

$$\langle \vec{H}_L \rangle_1 = (93, 93, 320) \text{ kG}$$

$$\langle \vec{H}_D \rangle_1 = (15, 15, -5) \text{ kG}$$

$\langle \vec{H}_S \rangle_1$ is largely cancelled by $\langle \vec{H}_L \rangle_1$ at very low temperatures, but since $\vec{H}_L$ decreases more rapidly in magnitude with increasing temperatures than $\vec{H}_S$ the cancellation decreases thereby increasing the net magnitude of $\vec{H}$ with increasing temperatures. The ground state wave function is

$$\begin{aligned} \Phi = & 0.088 \psi_1 \chi_0 + 0.092 (-1 + i) \psi_0 \chi_2 - 0.312 \psi_0 \chi_1 \\ & - 0.095 (1 + i) \psi_0 \chi_0 + 0.873 \psi_{-1} \chi_2 + 0.212 (1 + i) \psi_{-1} \chi_1, \end{aligned}$$

where $\psi_i \chi_j$ components, which are very small, are neglected. The main contribution comes from the $\psi_{-1} \chi_2$ state. Since $\frac{e^2 q Q}{2}$ is -1.876 mm/sec for a ψ_{-1} state, the low-temperature value of -1.32 mm/sec obtained by direct analysis from Mössbauer spectra can be easily understood from the ground state wave function. In the column 7 of Table 5, $\frac{e^2 q Q}{2}$ for each of 15 split levels below 100°K is shown. Since the first excited state Φ_2 gives a large positive value of 2.870 mm/sec for $\frac{e^2 q Q}{2}$ in contrast to the negative ground state value of -1.348 mm/sec, $\frac{e^2 q Q}{2}$ decreases very rapidly with increasing temperature (See Fig. 23).

It may be mentioned that Siegwarth²² used an IBM computer subroutine which can only diagonalize real matrices, but since the actual Hamiltonian was a complex Hermitian matrix, he used a trick of

rotating the whole crystal by a certain angle to get the eigenvectors and eigenvalues, thereby complicating the problem. We use a computer program⁴⁹, however, which can diagonalize any $N \times N$ Hermitian matrix ($N \leq 40$), and we diagonalized our Hermitian matrices without using this involved technique.

B. CoO(II)

Mössbauer spectra of CoO(II) at low temperatures are six-line patterns (Fig. 24), and almost purely magnetic. The hyperfine lines are broadened, however, which may be due to a quadrupole interaction with a random electric field gradient. The low temperature values of the magnetic hyperfine field is 553 kG which is typical of Fe^{3+} . The Fe^{3+} ions in CoO(II) are thought to originate from the trapping of electrons by anion vacancies discussed in detail in our preceding paper. The temperature-dependence of the magnetic hyperfine field follows a Brillouin function for $S = 3/2$ only approximately (Fig. 25). One noteworthy thing is that as the temperature increases a broad unsplit line grows in addition to the usual six-finger pattern and becomes a relatively narrow single line as the temperature approaches the Néel point. This anomaly and the line broadening of Mössbauer spectra were discussed in detail in Section V A.

C. CoO(I, II)

As shown in Section III and Section V CoO(I, II) is a simple mixture of CoO(I) and CoO(II) at low temperatures. At elevated temperatures, however, anion vacancies appear to dissociate from form II and disperse into form I in increasing numbers with increasing

Fig. 24. Mössbauer hyperfine pattern of CoO(II) at various temperatures. A 1.0 mg/cm^2 $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10 \text{ H}_2\text{O}$ absorber was used.

Fig. 25. Temperature dependence of the magnetic hyperfine field at Fe^{57} nuclei in CoO(II) . The solid curve shows Brillouin function for $S = 3/2$.

temperature. Therefore, the Mössbauer spectra of CoO(I, II) consist of Fe^{2+} lines and Fe^{3+} lines as shown in Fig. 26. The temperature-dependence of the magnetic hyperfine field and quadrupole interaction of Fe^{2+} in $\text{CoO(I, II)}_{\text{C,T}}$ ($\text{C} \leq 20\%$) is found to be the same as that of Fe^{57} in CoO(I) (compare Fig. 27 with Fig. 19). In particular, we found the following values of 77°K :

$$|H| = 150 \text{ kG}, \frac{e^2qQ}{2} = -1.01 \text{ mm/sec.}$$

$$\theta = 39.5^\circ, P = -0.33$$

Wertheim², and later Bhide and Shenoy⁴ reported that a satisfactory fit was found at 78°K for

$$|H| = 180 \text{ kG}, \frac{e^2qQ}{2} = 31 \text{ MC/sec} = 2.7 \text{ mm/sec}$$

$$\theta = 90^\circ, P = 0.35.$$

These results are not in agreement with our findings. For comparison we list Wertheim's spectra at 78°K in Fig. 28. When one compares the spectra of Wertheim with our Fig. 18 and Fig. 26, it appears that he assigned only one line to the three lines (No. 2, No. 3, and No. 4) shown in Fig. 18. The magnetic hyperfine field of Fe^{3+} in $\text{CoO(I, II)}_{\text{C,T}}$ ($\text{C} \leq 20\%$) has nearly the same value at low temperatures as that of CoO(II) , even though its Neel temperature is somewhat higher than that found for CoO(II) , and in fact corresponds to that of CoO(I) (Fig. 27), as was explained in Section V A.

Fig. 26. Mössbauer spectra of CoO(I, II) below the Néel temperature. A 0.75 mg/cm^2 $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10 \text{H}_2\text{O}$ absorber was used.

Fig. 27

Temperature dependence of the magnetic hyperfine field for Fe^{2+} and Fe^{3+} ions in CoO(I, II) . The solid curve on the points of Fe^{2+} is the theoretical curve of CoO(I) and the solid curve on the points of Fe^{3+} is only a visual fit.

Fig. 27

Fig. 28

Mössbauer spectra of CoO(I, II) at 78°K and room temperature reproduced from G. K. Wertheim [Phys. Rev. 124, 764 (1961)].

Fig. 28

IX. DISCUSSION

We proposed a model for cobaltous oxides based on the existence of two distinct structural forms. CoO(I) has the perfect NaCl structure, and CoO(II) has an NaCl structure with half of the cation and anion sites vacant. CoO(I, II) is a simple mixture of these two forms at 0°K , but is not a simple mixture at higher temperatures, where anions from clusters of form II disperse into form I.

Our proposed model was supported by the following observed properties.

1. Stoichiometry measurements, which gave $\text{CoO}_{1.00 \pm 0.05}$ for CoO(I) , CoO(II) , and CoO(I, II) show that all of our cobaltous oxide samples had the correct chemical composition of one cobalt and one oxygen, and the composition of CoO(II) is consistent with a highly vacated structure, with equal numbers of cation and anion vacancies.

2. Density measurements indicate that the density of CoO(II) is about half the value of CoO(I) , which strongly supports the proposed picture of the CoO(II) structure.

3. Mössbauer spectra which show pure Fe^{2+} lines for CoO(I) , pure Fe^{3+} lines for CoO(II) , and both $3+$ and $2+$ lines for the CoO(I, II) is in accord with our model and explains the mechanism by which charge compensation is achieved, i.e., anion vacancies can trap electrons resulting in Fe^{3+} .

4. The observed oxidation property, that CoO(II) absorbs oxygen very rapidly, but CoO(I) does not, also indicates a vacated structure for CoO(II) .

5. The irreversible conversion of CoO(II) to CoO(I) above 300°C in an inert atmosphere demonstrates that the metastable state of CoO(II) tends to convert to the stable state CoO(I) , upon receiving sufficient thermal energy.

6. The quenching of CoO(I, II) from high temperature, which enhanced the Fe^{2+} component of the Mössbauer pattern, indicates that strong stresses at elevated temperatures can cause the porous structure of form II to transform into form I.

7. A much lower Mössbauer characteristic Debye temperature of 320°K for CoO(II) compared with 510°K for CoO(I) can be explained on the basis of our model, which would indicate only half of the covalent bonds per ion in CoO(II) as is found in CoO(I) .

8. While both pure CoO(I) and CoO(II) had decreasing f-factors with increasing temperature, except for possible anomalous increases at the Néel temperatures, the area under Fe^{3+} Mössbauer absorption line in CoO(I, II) increased with increasing temperature. This is attributed to an increasing number of anion vacancies dispersed into form I. The anion vacancy diffusion is not only supported by rapid oxygen absorption at room temperature in CoO(II) , but also is supported by the Fe^{3+} behavior in Mössbauer patterns, which follow the f-factor of CoO(I) at elevated temperatures instead of that of CoO(II) , and had the same Néel temperature as form I instead of that of pure form II.

9. X-ray diffraction patterns show identical line positions and relative intensities for pure CoO(I) and CoO(II), which is demanded by our model. The line broadening of CoO(II) patterns can be explained by assuming form II to consist of ordered domains of sizes not greater than $50\text{\AA}$ in CoO(II).

Wertheim² prepared a sample of CoO(I, II) which showed both Fe^{2+} and Fe^{3+} lines in its Mössbauer spectra, and he concluded that the Fe^{2+} line arose from stable states and Fe^{3+} was produced because the relaxation time for reaching electronic equilibrium following the emission of an Auger electron must be comparable to the $\text{Fe}^{57\text{m}}$ nuclear lifetime of 10^{-7} sec. The same kind of experiment was repeated and the same results as found by Wertheim were reported by Bhide and Shenoy⁴, who also found an increasing relative intensity for $\text{Fe}^{3+}/\text{Fe}^{2+}$ Mössbauer line with increasing temperature, and they proposed that the relaxation time for the conversion of Fe^{3+} to Fe^{2+} increases in CoO as the temperature is raised. We prepared CoO(I) which showed only Fe^{2+} lines over all temperatures (Fig. 10) and CoO(II) which showed only Fe^{3+} lines (Fig. 11). The fact that we could observe only Fe^{2+} over all temperatures for CoO(I) indicates that the observed Fe^{3+} is not connected with a temperature dependent relaxation mechanism such as that proposed by Bhide and Shenoy⁴. Therefore, it is both unnecessary and inadequate to assume that Fe^{3+} lines observed in the Mössbauer spectra arise from Auger aftereffects.

Triftshäuser and Craig^{11,14} also found no evidence for Auger aftereffects in CoO using delayed-coincidence Mössbauer experiments. They showed that the relative intensity ratio I^{3+}/I^{2+} remains

constant for all delay times studied. They proposed, however, that their data could be interpreted in terms of a small excess of cation vacancies in CoO. Our experimental results can not be explained by this model.

Triftshäuser and Craig's proposal, accounting for their results on the basis of small deviations from ideal stoichiometry, is essentially based on three things: the electrical conductivity measurements by Fisher and Tannhauser¹², absorber experiments, and x-ray determinations ascribable to the CoO (NaCl-type structure). The results of Fisher and Tannhauser can at best be taken to establish that variations in stoichiometry are possible. We, of course, do not question this point, and our studies of the oxidation of CoO(II) clearly proves that excess oxygen is possible when this oxide is made. The point which we would emphasize, however, is that our results firmly establish that these possible variations in stoichiometry, are not, in fact, the reason why the two basic Mössbauer patterns (those corresponding to CoO(I) and CoO(II)) are observed. As shown in Section V the results of the TC absorber experiments are not confirmed by our experiments. As explained in detail in Section VI the same line positions and relative intensities of x-ray diffraction patterns are not generally unique in the determination of crystal structures involving large densities of defects.

Another possible explanation for the existence of Fe^{3+} in some experiments is recoil aftereffects^{5,50}. The recoiling $\text{Fe}^{57\text{m}}$ nucleus, whose recoil energy is of the order of 3 eV when the neutrino accompanying K-capture is emitted, may cause a local rearrangement of the

lattice which may produce complex spectra of the type observed in many hydrated crystals. Since CoO(I) and CoO(II) have been isolated and their properties can be explained by the existence of two forms of cobaltous oxide, it is unnecessary to assume recoil aftereffects for this material, even though some evidence of recoil aftereffects exists in other compounds such as hydrated compounds⁵.

Our model of two forms of cobaltous oxide has explained many experimental results better than any of the other models proposed so far, but we have some unsettled points which should be investigated further. In order to explain the broad unresolved line seen in CoO(II) below the Néel temperature, we suggested that domain walls restrict the length of ordering. The existence and size of these domains was not convincingly established. Also, CoO(II) absorbed oxygen in the form of $\text{CoO(II)} \cdot n\text{O}$, but the limit of oxygen saturation was not determined.

Another important property which was not measured is the temperature required to achieve true thermodynamic equilibrium in experimentally accessible time intervals. While the large clusters of form II irreversibly transformed to form I above 600°K , smaller form II clusters appeared stable at least to temperatures of 1000°K . This shows that the cation vacancies are immobile up to these temperatures in contrast with the anion vacancies which are mobile above 200°K .

We have analyzed hyperfine Mössbauer spectra of CoO(I) , CoO(II) , and CoO(I, II) . In connection with this analysis we have developed a general formalism which can give H , $\frac{e^2qQ}{2}$, θ , ϕ , and η from Mössbauer data by diagonalizing the interaction matrix related to the first

excited state of Fe^{57} nuclei. Our formalism has simpler expressions for the intensity ratio for the 8 lines than others reported in the literature^{39,40}, and requires diagonalization of only one 4×4 matrix. Mössbauer spectra of CoO(I) consist of pure Fe^{2+} lines, and were fitted with 8 lines at each temperature to give the temperature-dependence of H , $e^2qQ/2$, θ , η , and ϕ . ϕ is always -90° , and θ and η are approximately independent of temperature ($42^\circ \pm 5^\circ$ and 0.40 ± 0.05 respectively). The quadrupole interaction increases with decreasing temperature, but unexpectedly, the magnetic hyperfine field decreases with decreasing temperature. The tendency for the magnetic hyperfine field to decrease and the quadrupole interaction to increase with decreasing temperature, as well as temperature dependences of θ , η and ϕ can be explained by crystal field theory on the basis of temperature dependent variations in the statistical population of the perturbed 15 levels originating from the d_e level of Fe^{2+} . The values of H , $\frac{e^2qQ}{2}$, η , θ , and ϕ determined from Mössbauer spectra by diagonalizing the 4×4 magnetic and quadrupole Hamiltonian matrix are fitted very closely by those determined by crystal field theory under the assumption of the spin-orbit coupling, Heisenberg exchange interaction, and tetragonal crystalline field (See Figs. 19 through 22). Points with error bars are determined by diagonalizing the 4×4 interaction matrix to fit Mössbauer spectra, and represent the estimated confidence in this fitting. The solid curves are determined from crystal field theory. In this fitting, we adjusted various parameters, which turned out to be in reasonable agreement with those reported by others: $\langle r^{-3} \rangle = 4.4$ a.u. and $Q = 0.21$ b are essentially

the same as those reported by others^{45,48}. $H_c = -488$ kG is also nearly the same as -500 kG reported by Okiji and Kanamori⁴⁸. The covalency factor α^2 for many ferrous compounds⁴⁵ are reported to be between 0.6 and 0.8, and our adjusted covalency factor of 0.69 is also in this region. This implies a spin orbit coupling constant $\lambda = \alpha^2 \lambda_o = 102.3^\circ \text{K}$. The spin direction of $[\bar{1}\bar{1}3]$ (that is 25° from the c-axis) is nearly the same as the 27.3° value reported by van Laar²⁰, even though a comparison with these results are of limited value, because most samples of cobaltous oxides used by people in the past were probably CoO(I, II) instead of pure CoO(I) .

Many experiments on cobaltous oxide have been performed especially in neutron diffraction studies, conductivity studies, and x-ray studies. Now it is likely that many of these experiments were carried out using CoO(I, II) , and not the supposed CoO(I) with the perfect NaCl structure. Therefore, it is recommended that any future experiments on cobaltous oxide should be done after knowing its composition. There is also no reason why our proposed model may not be applied to other transition metal oxides such as NiO . We think that it is likely that similar effects can be found in NiO .

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APPENDIX A

THE HAMILTONIAN OF AN Fe^{57} ION

IN A CoO(I) CRYSTAL

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In this appendix we will give a brief discussion of the origin of each term in the perturbation Hamiltonian, representing the net perturbation from the free Fe^{57} ion due to interactions in a CoO(I) crystallite. The operator representing this perturbation can be written as

$$V_c + \lambda \vec{L} \cdot \vec{S} - 2 \sum_i J_i \vec{S}_i \cdot \vec{S} + \lambda \Delta (3I_z^2 - 2), \quad (\text{A1})$$

$$\text{where } V_c = A_4^0 r^4 \left\{ Y_4^0(\theta, \phi) + \left(\frac{5}{14}\right)^{\frac{1}{2}} [Y_4^4(\theta, \phi) + Y_4^{-4}(\theta, \phi)] \right\}, \quad (\text{A2})$$

A_4^0 is a constant, (r, θ, ϕ) are the spherical polar coordinates of a point with the Fe^{57} nucleus at the origin, and the Y's are the spherical harmonics.

The first term in eq. (A1) represents the energy due to the cubic electrostatic field originating from all oxygen ions and other ions. Assuming that the charge density of all the other ions is zero over the region of an Fe^{2+} ion, we can write the potential due to the

outside ions in terms of spherical harmonics, Y_ℓ^m , as

$$V = \sum_{\ell, m} A_\ell^m r^\ell Y_\ell^m(\theta, \phi), \quad (A3)$$

because V satisfies Laplace's equation over the region of the Fe^{2+} ion. If we neglect mixing of the ground state configuration, 5D , with the excited state configurations which are higher by about $20,000 \text{ cm}^{-1}$ than 5D , all matrix elements of V involve the integrals

$$\int \psi_{3d}^* r^\ell Y_\ell^m \psi_{3d}' d\vec{r}, \quad (A4)$$

where ψ_{3d} and ψ_{3d}' are 3d orbitals. The product of the d-functions ψ_{3d} and ψ_{3d}' transforms according to⁵³

$$D^{(2)} \times D^{(2)} = D^{(4)} + D^{(3)} + D^{(2)} + D^{(1)} + D^{(0)},$$

where $D^{(\ell)}$ represents ℓ -th irreducible representation of the full rotation group, and so matrix elements (A4) are zero for $\ell > 4$.

Similarly Y_ℓ^m must have even parity (ℓ even) because the product $\psi_{3d}^* \psi_{3d}'$ has even parity. The term $\ell = 0$ can also be dropped because it is an additive constant and is of no importance in the present analysis. Taking the polar axis along the [001] direction and applying the rotation operator $R_z(\frac{\pi}{2})$ to the (A3), we get

$$R_z(\frac{\pi}{2})V = e^{i\frac{\pi}{2}\ell z} V = \sum_{\ell, m} A_\ell^m r^\ell e^{i\frac{\pi}{2}m} Y_\ell^m. \quad (A5)$$

Since the z-axis is a 4-fold axis of a CoO(I) crystallite, V should be equal to $e^{i\frac{\pi}{2}\ell_z} V$. Thus, we get from eqs. (A3) and (A5)

$$A_{\ell}^m = A_{\ell}^m e^{i\frac{\pi}{2}m}$$

or

$$(1 - e^{i\frac{\pi}{2}m}) A_{\ell}^m = 0. \quad (A6)$$

In order that A_{ℓ}^m is not zero, m should be zero or a multiple of 4.

Thus V takes the form

$$V = A_2^0 r^2 Y_2^0(\theta, \phi) + A_4^0 r^4 Y_4^0(\theta, \phi) + A_4^4 r^4 Y_4^4(\theta, \phi) + A_4^{-4} r^4 Y_4^{-4}(\theta, \phi). \quad (A7)$$

Expressing V in terms of rectangular coordinates, we get

$$\begin{aligned} V = & A_2^0 \frac{1}{4} \left(\frac{5}{\pi}\right)^{\frac{1}{2}} (3z^2 - r^2) + A_4^0 \frac{1}{16} \left(\frac{9}{\pi}\right)^{\frac{1}{2}} (35z^4 - 30z^2 r^2 + 3r^4) \\ & + A_4^4 \left(\frac{9}{4\pi}\right)^{\frac{1}{2}} \left(\frac{35}{128}\right)^{\frac{1}{2}} (x+iy)^4 + A_4^{-4} \left(\frac{9}{4\pi}\right)^{\frac{1}{2}} \left(\frac{35}{128}\right)^{\frac{1}{2}} (x-iy)^4. \end{aligned} \quad (A8)$$

Since reflection in the xz-plane (which means $y \rightarrow -y$) transforms Y_4^4 into Y_4^{-4} , while leaving Y_4^0 and Y_2^0 unchanged, we get $A_4^4 = A_4^{-4}$, and V takes the form

$$\begin{aligned} V = & A_2^0 \frac{1}{4} \left(\frac{5}{\pi}\right)^{\frac{1}{2}} (3z^2 - r^2) + A_4^0 \frac{3}{16} \left(\frac{1}{\pi}\right)^{\frac{1}{2}} (35z^4 - 30z^2 r^2 + 3r^4) \\ & + A_4^4 \frac{3}{8} \left(\frac{35}{2\pi}\right)^{\frac{1}{2}} (x^4 - 6x^2 y^2 + y^4). \end{aligned} \quad (A9)$$

Neglecting the small tetragonal distortion of CoO(I) , for the moment, and applying a 120° rotation about the threefold axis, i.e., the $[1,1,1]$ direction, we find

$$A_4^4 = \sqrt{\frac{5}{14}} A_4^0, \text{ and } A_2^0 = 0. \quad (\text{A10})$$

Substituting (A10) into (A7), we obtain the cubic field term V_c in (A1). Matrix elements of V_c in the representation $Y_2^m (m=0, \pm 1, \pm 2)$ are calculated in a straightforward way. This matrix is

	Y_2^2	Y_2^{-2}	Y_2^1	Y_2^0	Y_2^{-1}
Y_2^2	C	5C	0	0	0
Y_2^{-2}	5C	C	0	0	0
Y_2^1	0	0	-4C	0	0
Y_2^0	0	0	0	6C	0
Y_2^{-1}	0	0	0	0	-4C

where $C = \frac{1}{14} A_4^0 \langle r^4 \rangle / \sqrt{\pi}$. By diagonalizing the above matrix one can find the following two energy levels, d_e and d_y :

level	cubic field energy shift	eigenfunctions
d_y	6C	$Y_2^0, (Y_2^2 + Y_2^{-2}) / \sqrt{2}$
d_e	-4C	$Y_2^1, Y_2^{-1}, (Y_2^2 - Y_2^{-2}) / \sqrt{2}$

Since the energy separation between d_e and d_y is generally of order of $10,000 \text{ cm}^{-1}$, we can neglect the d_y level for present purposes. The d_e functions are then given by

$$\begin{aligned}\psi_1 &= Y_2^{-1}, \\ \psi_0 &= (Y_2^2 - Y_2^{-2}) / \sqrt{2}, \\ \psi_{-1} &= -Y_2^1.\end{aligned}\tag{A11}$$

These functions behave like the eigen functions of the angular momentum $l=1$ if we put $\vec{l} = -\vec{L}$, where $\vec{L}$ is the true angular momentum and $\vec{l}$ can be considered as a pseudoangular momentum. This is evident when we calculate the matrices $\langle \psi_i | \vec{l} | \psi_j \rangle$ ($i, j = 1, 0, -1$), by using $\vec{l} = -\vec{L}$ and (A11). We get

$$\begin{aligned}\tilde{l}_+ &= \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}, \quad \tilde{l}_- = \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix}, \\ \tilde{l}_z &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.\end{aligned}\tag{A12}$$

These are exactly the matrices for a system with unit angular momentum.

Including the small tetragonal distortion of CoO(I) below the Néel temperature, we get an additional term which is proportional to

$3z^2 - r^2$ (see (A9)). Since $3z^2 - r^2$ is proportional to $3l_z^2 - l(l+1)$ in the $l=1$ manifold, we get the fourth term in (A1).

The second term in (A1) represents the spin-orbit coupling, which is due to the interaction of the magnetic moment of the electron with the magnetic field set up by its motion. Since this effect is entirely relativistic only the Dirac relativistic quantum theory can give a complete analysis. The result of the theory for a spherically symmetric potential $V(r)$ is⁵⁴

$$\mathcal{H}_{so} = \frac{1}{2m^2 c^2} \left(\frac{1}{r} \frac{dV}{dr} \right) \vec{l} \cdot \vec{s},$$

where m is the electron mass, c is the velocity of light, and r is the distance from the nucleus to the electron. $\vec{l}$ and $\vec{s}$ are the orbital and spin angular momenta of the electron, respectively. For several electrons, assuming that each electron is in an approximately spherically symmetric potential $V(r_i)$, $\mathcal{H}_{so}$ becomes

$$\mathcal{H}_{so} = \frac{1}{2m^2 c^2} \sum_i \frac{1}{r_i} \frac{dV(r_i)}{dr_i} \vec{l}_i \cdot \vec{s}_i.$$

We make the substitution

$$\int \frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV}{dr} R^2(r) r^2 dr = \xi$$

where $R(r)$ is the radial wave function of the electron. $\mathcal{H}_{so}$ is then rewritten as

$$\mathcal{H}_{so} = \sum_i \xi_i \vec{l}_i \cdot \vec{s}_i$$

Putting $\vec{L} = \sum_i \vec{l}_i$ and $\vec{S} = \sum_i \vec{s}_i$, and assuming Russel-Saunders coupling, we can express $\mathcal{H}_{so}$ in terms of $\vec{L}$ and $\vec{S}$ in the following way. Choosing a typical term $\xi_i \vec{l}_i \cdot \vec{s}_i$ (we will drop subscript i for the moment), and taking two states specified by $|\text{LSM}_L M_S\rangle$ and $|\text{LSM}'_L M'_S\rangle$, we get the following matrix element

$$\begin{aligned}
 & \langle \text{LSM}_L M_S | \xi \vec{l} \cdot \vec{s} | \text{LSM}'_L M'_S \rangle \\
 &= \sum_{m=0,\pm 1} \xi \langle \text{LSM}_L M_S | (-1)^m l_m s_{-m} | \text{LSM}'_L M'_S \rangle \\
 &= \xi \langle L || l || L \rangle \langle S || s || S \rangle \sum_m (-1)^m \langle \text{LM}'_L 1m | \text{LM}_L \rangle \langle \text{SM}'_S 1-m | \text{SM}_S \rangle, \quad (\text{A13})
 \end{aligned}$$

where l_m and s_m are defined by

$$l_{\pm 1} = \mp \frac{1}{\sqrt{2}} (l_x \pm i l_y), \quad l_0 = l_z,$$

$$s_{\pm 1} = \mp \frac{1}{\sqrt{2}} (s_x \pm i s_y), \quad s_0 = s_z,$$

and the Wigner-Eckart theorem was used to get the last expression.

$\langle L || l || L \rangle$ and $\langle S || s || S \rangle$ are the reduced matrix element independent of the magnetic quantum numbers M_L, M'_L, M_S, M'_S, m . $\langle \text{LM}'_L 1m | \text{LM}_L \rangle$ and $\langle \text{SM}'_S 1-m | \text{SM}_S \rangle$ are Clebsch-Gordan coefficients. On the other hand, one obtains for the matrix element of $\vec{L} \cdot \vec{S}$

$$\begin{aligned}
 & \langle \text{LSM}_L M_S | \vec{L} \cdot \vec{S} | \text{LSM}'_L M'_S \rangle \\
 &= \sum_{m=0,\pm 1} \langle \text{LSM}_L M_S | (-1)^m L_m S_{-m} | \text{LSM}'_L M'_S \rangle \\
 &= \langle L || L || L \rangle \langle S || S || S \rangle \sum_m (-1)^m \langle \text{LM}'_L 1m | \text{LM}_L \rangle \langle \text{SM}'_S 1-m | \text{SM}_S \rangle. \quad (\text{A14})
 \end{aligned}$$

Comparing (A14) with (A13), one obtains

$$\begin{aligned} & \langle LSM_L M_S | \xi \vec{l} \cdot \vec{s} | LSM'_L M'_S \rangle \\ &= a \langle LSM_L M_S | L \cdot S | LSM'_L M'_S \rangle, \end{aligned}$$

where a is a constant independent of the magnetic quantum numbers.

Similarly, we can get

$$\begin{aligned} & \langle LSM_L M_S | \sum_i \xi_i \vec{l}_i \cdot \vec{s}_i | LSM'_L M'_S \rangle \\ &= \lambda \langle LSM_L M_S | \vec{L} \cdot \vec{S} | LSM'_L M'_S \rangle, \end{aligned}$$

where λ is a constant independent of the magnetic quantum numbers,

depending essentially on the radial wave function in an electronic

configuration with only one L and one S . However, as shown in

Sec. VIIB, the actual wavefunctions of Fe^{2+} ion in the cubic field

are linear combinations of these states $|LSM_L M_S\rangle (M_L, M_S = \pm 1, \pm 2)$.

Therefore, a matrix element between any two actual wave functions can

be expressed in a linear combination of the above matrices between

the pure states $|LSM_L M_S\rangle (M_L, M_S = 0, \pm 1, \pm 2)$. Since the radial

wave function of an Fe^{2+} ion will change in a $CoO(I)$ crystallite due

to covalency effects, a resulting change of λ is expected. Owen⁵⁵

has observed that the effective spin-orbit coupling constant is some-

what smaller for an ion in a crystal than for a free ion. He showed

that it was plausible to relate the spin-orbit coupling constant to

the covalency factor through the relation

$$\lambda = \alpha^2 \lambda_0,$$

where the covalency factor, α^2 , is generally between 0.6 and 0.9.

The third term in (A1) represents the Heisenberg exchange interaction and can be derived in the following way⁵⁶: consider exactly N electrons occupying exactly N different, orthogonal orbital states $f_n(\vec{r})$. It is assumed that each orbital contains one electron, i.e., the electrons may be localized. The Hamiltonian is

$$\mathcal{H} = \sum_i \left[\frac{p_i^2}{2m_i} + V(\vec{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \quad (\text{A15})$$

the summations being over the N electrons. If the orbitals f_n are orthogonal, then the kinetic energy and the potential energy $V(\vec{r}_i)$ resulting from ion cores, etc., do not depend on the spin orientations, and we have only to study the Coulomb interaction $e^2/|\vec{r}_i - \vec{r}_j|$. For this problem we will use second quantization following

Anderson⁵⁶, and so treat the problem in terms of occupation numbers rather than explicit determinantal wave functions. This older approach is discussed in detail in many places⁵⁷. Each orbital $f_n(\vec{r})$ has two sets of creation and annihilation operators, C_{n+}^* and C_{n+} , C_{n-}^* and C_{n-} , which refer to the states of up and down spin, respectively. The requirement that one and only one electron may occupy orbital n means that

$$n_{n+} + n_{n-} = C_{n+}^* C_{n+} + C_{n-}^* C_{n-} = 1, \quad (\text{A16})$$

where n_{n+} and n_{n-} represent the occupation numbers of the states of up and down spin. The spin operators $\vec{s}_n$ may be represented as

follows:

$$\begin{aligned}
 s_n^+ &= s_n^x + i s_n^y = C_{n+}^* C_{n-}, \\
 s_n^- &= s_n^x - i s_n^y = C_{n-}^* C_{n+}, \\
 2s_n^z &= n_{n+} - n_{n-}.
 \end{aligned} \tag{A17}$$

Equation (A17) may be verified by observing that the above combinations have the proper raising and lowering properties on wave functions satisfying (A16), e.g.,

$$\begin{aligned}
 s_n^+ |n_-\rangle &= C_{n+}^* C_{n-} |n_-\rangle = C_{n+}^* |0\rangle = |n_+\rangle, \\
 s_n^- |n_+\rangle &= C_{n-}^* C_{n+} |n_+\rangle = C_{n-}^* |0\rangle = |n_-\rangle, \text{ etc.}
 \end{aligned}$$

The Coulomb interaction term in (A15) can be written as follows by using a formula⁵⁶ derived in the second quantization formalism:

$$\begin{aligned}
 V &= \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{n_1 n_2 n_3 n_4} C_{n_1 \sigma'}^* C_{n_2 \sigma}^* C_{n_3 \sigma} C_{n_4 \sigma'} \\
 &\times \int d\vec{r} \int d\vec{r}' f_{n_1}^*(\vec{r}') f_{n_2}^*(\vec{r}) \frac{e^2}{|\vec{r} - \vec{r}'|} f_{n_4}(\vec{r}') f_{n_3}(\vec{r}). \tag{A18}
 \end{aligned}$$

If we ignore the possibility of a transfer of electrons from one orbital to another, the pair (n_1, n_2) must be the same as the pair (n_3, n_4) . This leaves us with only two terms corresponding to

$$(n_1 = n_3, n_2 = n_4) \text{ and } (n_1 = n_4, n_2 = n_3), \text{ i.e.,}$$

$$V = \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{n, n'} (n_{n'\sigma'} n_{n\sigma} K_{nn'} + C_{n'\sigma'}^* C_{n\sigma} C_{n'\sigma} C_{n\sigma'} J_{nn'}), \quad (\text{A19})$$

$$\text{where } K_{nn'} = \int d\vec{r} \int d\vec{r}' |f_n(\vec{r})|^2 e^2 |\vec{r} - \vec{r}'|^{-1} |f_{n'}(\vec{r}')|^2,$$

and

$$J_{nn'} = \int d\vec{r} \int d\vec{r}' f_n^*(\vec{r}') f_n(\vec{r}') f_{n'}^*(\vec{r}) f_{n'}(\vec{r}) e^2 |\vec{r} - \vec{r}'|^{-1}.$$

The first term is simply the ordinary Coulomb repulsion between the electrons in the two orbitals, and is also not spin-dependent. Neglecting this term and using (A16) and (A17), we get

$$\begin{aligned} V &= \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{n, n'} C_{n'\sigma'}^* C_{n\sigma} C_{n'\sigma} C_{n\sigma'} J_{nn'} \\ &= \frac{1}{2} \sum_{n, n'} J_{nn'} [C_{n'+}^* C_{n+}^* C_{n'+} C_{n+} + C_{n'+}^* C_{n-}^* C_{n'+} C_{n-} \\ &\quad + C_{n'-}^* C_{n+}^* C_{n'-} C_{n+} + C_{n'-}^* C_{n-}^* C_{n'-} C_{n-}] \\ &= -\frac{1}{2} \sum_{n, n'} J_{nn'} [n_{n'+} n_{n+} + n_{n'-} n_{n-} + s_{n'}^+ s_n^- + s_{n'}^- s_n^+] \\ &= -\frac{1}{2} \sum_{n, n'} J_{nn'} [\frac{1}{2} + 2s_n^z s_{n'}^z + s_{n'}^+ s_n^- + s_{n'}^- s_n^+] \\ &= -\sum_{n, n'} J_{nn'} [\frac{1}{4} + \vec{s}_{n'} \cdot \vec{s}_n] \\ &= -\sum_{n > n'} J_{nn'} [\frac{1}{2} + 2\vec{s}_{n'} \cdot \vec{s}_n]. \end{aligned}$$

This is the Heisenberg exchange interaction energy. The spin-independent term is again of no interest and is neglected in the analysis. Thus far, we have assumed that the orbitals $f_n(\vec{r})$ are orthogonal and the spins are localized. Various kinds of objections⁵⁶ to the Heisenberg Hamiltonian have been raised, but it is a fair approximation for insulating materials, because spins are reasonably localized in these materials.

APPENDIX B

THE MAGNETIC HYPERFINE FIELD AT A NUCLEUS IN A CRYSTAL

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In this appendix, we will derive the magnetic hyperfine field at a nucleus in a crystal. An electron of mass m and charge e in the electromagnetic field $(\phi, \vec{A})$ has the following Hamiltonian:

$$\mathcal{H} = \frac{1}{2m} (\vec{p} - \frac{e}{c} \vec{A})^2 - \vec{\mu}_e \cdot \vec{H} + e\phi, \quad (\text{B1})$$

where $\vec{\mu}_e$ is the electron magnetic moment. $\vec{\mu}_e$ can be written in terms of the electron spin $\vec{s}$ as follows,

$$\vec{\mu}_e = 2 \cdot \frac{e\hbar}{2mc} \vec{s} = 2\mu_B \vec{s}, \quad (\text{B2})$$

where μ_B is the Bohr magneton.

When $\vec{A}$ is produced by a nuclear magnetic moment $\vec{\mu}_n$, $\vec{A}$ can be written as:

$$\vec{A} = \frac{\vec{\mu}_n \times \vec{r}}{r^3} = \nabla \times \left(\frac{\vec{\mu}_n}{r} \right), \quad (\text{B3})$$

where $\vec{r}$ is the vector distance from the nucleus to the electron. Expanding (B1) and neglecting the A^2 term, we get

$$\mathcal{H} = \frac{p^2}{2m} + e\phi - \frac{e}{2mc} (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) - \vec{\mu}_e \cdot \vec{H}. \quad (\text{B4})$$

The first and second terms are the kinetic and electrostatic potential energies of the electron, respectively. The third and fourth terms are the interaction terms between the electron and the nuclear magnetic moment. Since $\nabla \cdot \vec{A} = \nabla \cdot \nabla \times \left(\frac{\vec{\mu}_n}{r} \right) \equiv 0$, the first interaction

term can be written as:

$$\begin{aligned} \mathcal{H}_1' &= -\frac{e}{2mc} (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) = -\frac{e}{mc} \vec{A} \cdot \vec{p} = -\frac{e}{mc} \frac{\vec{\mu}_n \times \vec{r}}{r^3} \cdot \vec{p} \\ &= -\frac{e}{mc} \frac{\vec{r} \times \vec{p}}{r^3} \cdot \vec{\mu}_n = -\frac{e\hbar \vec{\ell} \cdot \vec{\mu}_n}{mc r^3} = -\left(2\mu_B \frac{\vec{\ell}}{r^3}\right) \cdot \vec{\mu}_n, \end{aligned} \quad (\text{B5})$$

where we have introduced the orbital angular momentum $\vec{\ell} = \vec{r} \times \vec{p}$.

The second interaction term can be calculated with the aid of (B3):

$$\mathcal{H}_2' = -\vec{\mu}_e \cdot \vec{H} = -\vec{\mu}_e \cdot \nabla \times \vec{A} = -\vec{\mu}_e \cdot \nabla \times \nabla \times \frac{\vec{\mu}_n}{r}.$$

Using the vector identity $\nabla \times \nabla \times \vec{a} = \nabla (\nabla \cdot \vec{a}) - \nabla^2 \vec{a}$, we get

$$\mathcal{H}_2' = -(\vec{\mu}_e \cdot \nabla)(\vec{\mu}_n \cdot \nabla)\left(\frac{1}{r}\right) + (\vec{\mu}_e \cdot \vec{\mu}_n) \nabla^2 \frac{1}{r}. \quad (\text{B6})$$

Where $r \neq 0$ (p,d,...electrons except s-electron), $\nabla^2 \frac{1}{r} = 0$ and the first term can easily be calculated by performing the differentiation.

The result is

$$\begin{aligned} \mathcal{H}_2' &= -3 (\vec{\mu}_n \cdot \vec{r})(\vec{\mu}_e \cdot \vec{r})r^{-5} + (\vec{\mu}_e \cdot \vec{\mu}_n)r^{-3} \\ &= -\vec{\mu}_n \cdot 2\mu_B [3\vec{r}(\vec{s} \cdot \vec{r})r^{-5} - \vec{s}r^{-3}]. \end{aligned} \quad (\text{B7})$$

For an s electron, however, the condition $r \neq 0$ does not hold and (B6) has a singularity at the origin, due to the term $\frac{1}{r^3}$. To determine the effect of the operator (B6), it is convenient to examine the result of integration of the product of this quantity with a well-behaved function $f(\vec{r})$ in a small domain about $\vec{r}=0$. We write (B6) in

the form

$$\begin{aligned} \mathcal{H}_2^1 &= \frac{2}{3} (\vec{\mu}_e \cdot \vec{\mu}_n) \nabla^2 \left(\frac{1}{r} \right) - [(\vec{\mu}_e \cdot \nabla)(\vec{\mu}_n \cdot \nabla) - \frac{1}{3} (\vec{\mu}_e \cdot \vec{\mu}_n) \nabla^2] \left(\frac{1}{r} \right) \\ &= -\frac{8\pi}{3} (\vec{\mu}_e \cdot \vec{\mu}_n) \delta(\vec{r}) - [(\vec{\mu}_e \cdot \nabla)(\vec{\mu}_n \cdot \nabla) - \frac{1}{3} (\vec{\mu}_e \cdot \vec{\mu}_n) \nabla^2] \left(\frac{1}{r} \right), \end{aligned} \quad (B8)$$

where $\nabla^2 \left(\frac{1}{r} \right) = -4\pi \delta(\vec{r})$ was used.

The second term in (B8) (shown in square brackets) is a second order tensor in the coordinate space. To calculate the intergration mentioned above, $f(\vec{r})$ is expanded in spherical harmonics. Only spherical harmonics of order 2 will contribute to the angular integrations, and this vanishes at the origin as rapidly as r^2 . Thus the integration vanishes as r approaches zero in the following way.

$$\int \frac{1}{r} r^2 r^2 dr \rightarrow \int r dr \rightarrow 0.$$

Thus we get for an s-electron,

$$\mathcal{H}_2^1 = -\frac{16\pi}{3} \mu_B \vec{s} \delta(\vec{r}) \cdot \vec{\mu}_n. \quad (B9)$$

From (B5), (B7) and (B9) the magnetic hyperfine field at the nucleus due to the electron follows:

$$\begin{aligned} \vec{H} &= 2\mu_B r^{-3} \vec{l} + 2\mu_B [3\vec{r} (\vec{s} \cdot \vec{r}) r^{-5} - \vec{s} r^{-3}] \\ &\quad + \frac{16\pi}{3} \mu_B \vec{s} \delta(\vec{r}). \end{aligned} \quad (B10)$$

The last term exists only for s-electrons.

For an ion with an open subshell such as the 3d subshell of Fe^{2+} , (B10) can be generalized to

$$\begin{aligned} \vec{H} = & 2\mu_B \alpha^2 \langle r^{-3} \rangle \langle \vec{L} \rangle \\ & + 2\mu_B \alpha^2 \langle r^{-3} \rangle \langle \sum_i [3(\vec{r}_i/r_i)(\vec{s}_i \cdot \vec{r}_i/r_i) - \vec{s}_i] \rangle \\ & + \frac{16\pi}{3} \mu_B \langle \sum_j \vec{s}_j \delta(\vec{r}_j) \rangle, \end{aligned} \quad (\text{B11})$$

where $\vec{L}$ is the total orbital angular momentum of the ion, the sum in the second term is over the unclosed shell, and the sum in the third term is over the s-electrons. The averages in the first two terms refer to the unclosed shell, for example, the 3d electron shell of a transition element or the 4 f shell of a rare earth element. The covalency factor α^2 relates to reduction of $\langle r^{-3} \rangle$ due to the covalent bonding.

APPENDIX C

DIAGONALIZATION OF THE 15×15 PERTURBATION MATRIX
AND CALCULATION OF THE ORBITAL AND SPIN ANGULAR
MOMENTA, DIPOLAR TERM, AND ELECTRIC FIELD
GRADIENT IN THE ENERGY EIGENSTATES

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In this appendix the elements of the 15 x 15 interaction matrix are explicitly calculated, and the diagonalization of the matrix is carried out by a unitary transformation matrix, thereby giving eigen-energies and eigenfunctions. In this new basis, the orbital and spin angular momenta, dipolar term, and electric field gradient tensor are calculated.

When energies are expressed in units of the spin-orbit coupling constant $|\lambda|$, the interaction Hamiltonian $\mathcal{H}'$ can be written as:

$$\mathcal{H}' = \vec{l} \cdot \vec{S} - x \vec{M} \cdot \vec{S} - \Delta(3l_z^2 - 2), \quad (C1)$$

where $x = \beta \langle S_i \rangle$.

Expressing the angular momenta $\vec{l}$ and $\vec{S}$ in terms of raising and lowering operators $l_{\pm}$, $S_{\pm}$, and z-components l_z , S_z , we obtain for $\mathcal{H}'$

$$\begin{aligned} \mathcal{H}' = & \frac{l_+ S_- + l_- S_+}{2} + l_z S_z - x \left(\frac{M_+ S_- + M_- S_+}{2} + M_z S_z \right) \\ & - \Delta(3l_z^2 - 2), \end{aligned} \quad (C2)$$

where $M_{\pm} = M_x \pm iM_y = \sin \theta_0 (1 \pm i)/\sqrt{2}$, and $M_z = \cos \theta_0$.

15 wave functions Ψ_m ($m = 1, 2, \dots, 15$) will be labeled as follows:

$$\left. \begin{array}{lll} \Psi_1 = \psi_1 X_2 & \Psi_6 = \psi_0 X_2 & \Psi_{11} = \psi_{-1} X_2 \\ \Psi_2 = \psi_1 X_1 & \Psi_7 = \psi_0 X_1 & \Psi_{12} = \psi_{-1} X_1 \\ \Psi_3 = \psi_1 X_0 & \Psi_8 = \psi_0 X_0 & \Psi_{13} = \psi_{-1} X_0 \\ \Psi_4 = \psi_1 X_{-1} & \Psi_9 = \psi_0 X_{-1} & \Psi_{14} = \psi_{-1} X_{-1} \\ \Psi_5 = \psi_1 X_{-2} & \Psi_{10} = \psi_0 X_{-2} & \Psi_{15} = \psi_{-1} X_{-2} \end{array} \right\} \quad (C3)$$

Using the notation $\mathcal{H}'_{ij} = \langle \Psi_i | \mathcal{H}' | \Psi_j \rangle$ as a matrix element of $\mathcal{H}'$, we obtain the following non-zero elements:

$$\begin{aligned} \mathcal{H}'_{11} &= 2 - 2xM_z - \Delta, & \mathcal{H}'_{22} &= 1 - xM_z - \Delta, \\ \mathcal{H}'_{33} &= \mathcal{H}'_{1313} = -\Delta, & \mathcal{H}'_{44} &= -1 + xM_z - \Delta, \\ \mathcal{H}'_{55} &= -2 + 2xM_z - \Delta, & \mathcal{H}'_{66} &= -2xM_z + 2\Delta, \\ \mathcal{H}'_{77} &= -xM_z + 2\Delta, & \mathcal{H}'_{88} &= 2\Delta, \\ \mathcal{H}'_{99} &= xM_z + 2\Delta, & \mathcal{H}'_{1010} &= 2xM_z + 2\Delta, \\ \mathcal{H}'_{1111} &= -2 - 2xM_z - \Delta, & \mathcal{H}'_{1212} &= -1 - xM_z - \Delta, \\ \mathcal{H}'_{1414} &= 1 + xM_z - \Delta, & \mathcal{H}'_{1515} &= 2 + 2xM_z - \Delta, \\ \mathcal{H}'_{12} &= \mathcal{H}'_{45} = \mathcal{H}'_{67} = \mathcal{H}'_{910} = \mathcal{H}'_{1112} = \mathcal{H}'_{1415} = -xM_z, & \mathcal{H}'_{23} &= \mathcal{H}'_{34} \\ &= \mathcal{H}'_{23} = \mathcal{H}'_{89} = \mathcal{H}'_{1213} = \mathcal{H}'_{1314} = -\sqrt{6}xM_z/2, & \mathcal{H}'_{26} &= \mathcal{H}'_{59} = \mathcal{H}'_{711} \\ &= \mathcal{H}'_{1014} = \sqrt{2}, & \mathcal{H}'_{78} &= -\frac{\sqrt{6}}{2}xM_z, \mathcal{H}'_{37} = \mathcal{H}'_{48} = \mathcal{H}'_{812} = \mathcal{H}'_{913} = \sqrt{3}. \end{aligned} \quad (C4)$$

Before diagonalizing this 15×15 matrix we list the non-zero matrix elements, $\langle \Psi_n | \vec{L} | \Psi_m \rangle$, $\langle \Psi_n | \vec{S} | \Psi_m \rangle$, $\langle \Psi_n | \vec{h}_D | \Psi_m \rangle$, and $\langle \Psi_n | V_{ij} | \Psi_m \rangle$ ($n, m = 1, 2, \dots, 15, n \leq m$) for future convenience:

$$\left. \begin{aligned} \langle \Psi_m | L_x | \Psi_{m+5} \rangle &= -1/\sqrt{2}, \\ \langle \Psi_m | L_y | \Psi_{m+5} \rangle &= i/\sqrt{2}, \quad (m=1, 2, \dots, 10) \text{ and} \\ \langle \Psi_m | L_z | \Psi_m \rangle &= -\langle \Psi_{m+10} | L_z | \Psi_{m+10} \rangle = -1, \end{aligned} \right\} \quad (C5)$$

where $m = 1, 2, \dots, 15$.

$$\left. \begin{aligned} \langle \Psi_m | S_x | \Psi_{m+1} \rangle &= \begin{cases} 1 & \text{for } m = 1, 4, 6, 9, 11, 14 \\ \sqrt{6}/2 & \text{for } m = 2, 3, 7, 8, 12, 13, \end{cases} \\ \langle \Psi_m | S_y | \Psi_{m+1} \rangle &= -i \langle \Psi_m | S_x | \Psi_{m+1} \rangle, \\ & \quad (m = 1, 2, \dots, 14), \\ \langle \Psi_m | S_z | \Psi_m \rangle &= \begin{cases} 2 & \text{for } m = 1, 6, 11 \\ 1 & \text{for } m = 2, 7, 12 \\ -1 & \text{for } m = 4, 9, 14 \\ -2 & \text{for } m = 5, 10, 15. \end{cases} \end{aligned} \right\} \quad (C6)$$

For convenience of calculation xyz components of $\vec{h}_D$ can be written in terms of the spherical harmonics Y_2^m ($m = 0, \pm 1, \pm 2$) and $S_{\pm}$, S_z as

follows:

$$\begin{aligned}
 (h_D)_x &= \sqrt{\frac{\pi}{5}} (\sqrt{6} Y_2^{-2} - Y_2^0) s_+ \\
 &\quad + \sqrt{\frac{\pi}{5}} (\sqrt{6} Y_2^2 - Y_2^0) s_- \\
 &\quad + \sqrt{\frac{6\pi}{5}} (Y_2^{-1} - Y_2^1) s_z, \\
 (h_D)_y &= i\sqrt{\frac{\pi}{5}} (Y_2^0 + \sqrt{6} Y_2^{-2}) s_+ \\
 &\quad - i\sqrt{\frac{\pi}{5}} (Y_2^0 + \sqrt{6} Y_2^{+2}) s_- \\
 &\quad + i\sqrt{\frac{6\pi}{5}} (Y_2^1 + Y_2^{-1}) s_z \\
 (h_D)_z &= \sqrt{\frac{6\pi}{5}} Y_2^{-1} s_+ - \sqrt{\frac{6\pi}{5}} Y_2^1 s_- \\
 &\quad + 4\sqrt{\frac{\pi}{5}} Y_2^0 s_z
 \end{aligned} \tag{C7}$$

Using these expressions for calculation purpose, and denoting the matrix elements $\langle \Psi_i | (h_D)_x | \Psi_j \rangle$, $\langle \Psi_i | (h_D)_y | \Psi_j \rangle$, and $\langle \Psi_i | (h_D)_z | \Psi_j \rangle$ by h_{ij}^x , h_{ij}^y , and h_{ij}^z ($i, j, = 1, 2, \dots, 15, i < j$) for briefness, we get the following non-zero matrix elements:

$$\begin{aligned}
 h_{1\ 2}^x &= h_{4\ 5}^x = h_{11\ 12}^x = h_{14\ 15}^x = -\frac{1}{7}, \\
 h_{1\ 6}^x &= -h_{5\ 10}^x = -h_{6\ 11}^x = h_{10\ 15}^x = -3\sqrt{2}/7, \\
 h_{1\ 12}^x &= h_{4\ 15}^x = \frac{6}{7}, \\
 h_{2\ 3}^x &= h_{3\ 4}^x = h_{12\ 13}^x = h_{13\ 14}^x = -\sqrt{6}/14, \\
 h_{2\ 7}^x &= -h_{4\ 9}^x = -h_{7\ 12}^x = h_{9\ 14}^x = -3\sqrt{2}/14,
 \end{aligned} \tag{C8}$$

$$h_{2\ 13}^x = h_{3\ 14}^x = 3\sqrt{6}/7,$$

$$h_{6\ 7}^x = h_{9\ 10}^x = \frac{2}{7},$$

$$h_{7\ 8}^x = h_{8\ 9}^x = \sqrt{6}/7,$$

$$h_{1\ 2}^y = h_{4\ 5}^y = h_{11\ 12}^y = h_{14\ 15}^y = i/7,$$

$$h_{1\ 6}^y = -h_{5\ 10}^y = -h_{6\ 11}^y = h_{10\ 15}^y = 3\sqrt{2}i/7,$$

$$h_{1\ 12}^y = h_{4\ 15}^y = 6i/7,$$

$$h_{2\ 3}^y = h_{3\ 4}^y = h_{12\ 13}^y = h_{13\ 14}^y = \sqrt{6}i/14,$$

$$h_{2\ 7}^y = -h_{4\ 9}^y = -h_{7\ 12}^y = h_{9\ 14}^y = 3\sqrt{2}i/14,$$

$$h_{2\ 13}^y = h_{3\ 14}^y = 3\sqrt{6}i/7,$$

$$h_{6\ 7}^y = h_{9\ 10}^y = -2i/7,$$

$$h_{7\ 8}^y = h_{8\ 9}^y = -\sqrt{6}i/7,$$

(C9)

$$h_{1\ 1}^z = -h_{5\ 5}^z = -h_{7\ 7}^z = h_{9\ 9}^z = h_{11\ 11}^z = -h_{15\ 15}^z = \frac{4}{7},$$

$$h_{2\ 2}^z = -h_{4\ 4}^z = h_{12\ 12}^z = -h_{14\ 14}^z = \frac{2}{7},$$

$$h_{2\ 6}^z = h_{5\ 9}^z = -h_{7\ 11}^z = -h_{10\ 14}^z = -3\sqrt{2}/7,$$

$$h_{3\ 7}^z = h_{4\ 8}^z = -h_{8\ 12}^z = -h_{9\ 13}^z = -3\sqrt{3}/7,$$

$$h_{6\ 6}^z = -h_{10\ 10}^z = -8/7.$$

(C10)

The angular part of the electric field gradient tensor component V_{ij} may be written as

$$v_{ij} = 3 \frac{x_i}{r} \frac{x_j}{r} - \delta_{ij}, \quad (C11)$$

where $V_{ij} = -e\alpha^2 \langle r^{-3} \rangle v_{ij}$.

Expressing the operator v_{ij} in terms of the spherical harmonics Y_2^m ($m = 0, \pm 1, \pm 2$), one can get the following results.

$$\left. \begin{aligned} v_{11} &= -\sqrt{\frac{4\pi}{5}} Y_2^0 + \sqrt{\frac{6\pi}{5}} (Y_2^2 + Y_2^{-2}), \\ v_{12} &= -i \sqrt{\frac{6\pi}{5}} (Y_2^2 - Y_2^{-2}), \\ v_{13} &= -\sqrt{\frac{6\pi}{5}} (Y_2^1 - Y_2^{-1}), \\ v_{22} &= -\sqrt{\frac{4\pi}{5}} Y_2^0 - \sqrt{\frac{6\pi}{5}} (Y_2^2 + Y_2^{-2}), \\ v_{23} &= i \sqrt{\frac{6\pi}{5}} (Y_2^1 + Y_2^{-1}), \\ v_{33} &= 4 \sqrt{\frac{\pi}{5}} Y_2^0 \end{aligned} \right\} \quad (C12)$$

Using these expressions we evaluate the following non-zero matrix elements:

$$\left. \begin{aligned} \langle \Psi_m | v_{11} | \Psi_m \rangle &= \langle \Psi_{m+10} | v_{11} | \Psi_{m+10} \rangle = -\frac{1}{7}, \\ &\quad (m = 1, 2, 3, 4, 5), \\ \langle \Psi_m | v_{11} | \Psi_m \rangle &= \frac{2}{7}, \quad (m = 6, 7, 8, 9, 10), \\ \langle \Psi_m | v_{11} | \Psi_{m+10} \rangle &= \frac{3}{7}, \quad (m = 1, 2, 3, 4, 5), \end{aligned} \right\} \quad (C13)$$

$$\langle \Psi_m | v_{12} | \Psi_{m+10} \rangle = 3i/7, \quad (m = 1, 2, 3, 4, 5), \quad (C14)$$

$$\left. \begin{aligned} \langle \Psi_m | v_{13} | \Psi_{m+5} \rangle &= -3\sqrt{2}/14, \quad (m = 1, 2, 3, 4, 5), \\ \langle \Psi_m | v_{13} | \Psi_{m+5} \rangle &= 3\sqrt{2}/14, \quad (m = 6, 7, 8, 9, 10), \end{aligned} \right\} \quad (C15)$$

$$\left. \begin{aligned} \langle \Psi_m | v_{22} | \Psi_m \rangle &= \langle \Psi_{m+10} | v_{22} | \Psi_{m+10} \rangle = -\frac{1}{7}, \\ (m = 1, 2, 3, 4, 5), \\ \langle \Psi_m | v_{22} | \Psi_m \rangle &= \frac{2}{7}, \quad (m = 6, 7, 8, 9, 10), \\ \langle \Psi_m | v_{22} | \Psi_{m+10} \rangle &= -\frac{3}{7}, \quad (m = 1, 2, 3, 4, 5), \end{aligned} \right\} \quad (C16)$$

$$\left. \begin{aligned} \langle \Psi_m | v_{23} | \Psi_{m+5} \rangle &= 3\sqrt{2}i/14, \quad (m = 1, 2, 3, 4, 5), \\ \langle \Psi_m | v_{23} | \Psi_{m+5} \rangle &= -3\sqrt{2}i/14, \quad (m = 6, 7, \dots, 10), \end{aligned} \right\} \quad (C17)$$

$$\left. \begin{aligned} \langle \Psi_m | v_{33} | \Psi_m \rangle &= \frac{2}{7}, \quad (m = 1, 2, \dots, 5, 11, 12, \dots, 15), \\ \langle \Psi_m | v_{33} | \Psi_m \rangle &= -\frac{4}{7}, \quad (m = 6, 7, \dots, 10). \end{aligned} \right\} \quad (C18)$$

Diagonalizing the 15×15 matrix $\langle \Psi_m | \mathcal{H} | \Psi_{m'} \rangle$ ($m, m' = 1, 2, \dots, 15$) by an unitary transformation matrix $\tilde{A}$, we get the eigenvalues E_n and the corresponding eigenvectors Φ_n ($n = 1, 2, \dots, 15$).

$$\tilde{A}^{-1} \mathcal{H} \tilde{A} = \tilde{E}, \quad \tilde{A} = \| \tilde{a}_{ij} \|, \quad (C19)$$

$$\Phi_n = \sum_m \Psi_m a_{mn},$$

where $\tilde{E}$ is the diagonal matrix whose diagonal elements are

E_n ($n = 1, 2, \dots, 15$), the eigenenergies of the 15 split d_e states.

The orbital and spin angular momenta, dipolar term, and electric field gradient tensor components in the eigenstate Φ_n can be easily calculated in terms of a_{mn} ($m, n = 1, 2, \dots, 15$) in the following way.

Representing any one of the above operators as O we get the following expression as the expectation value of O in the eigenstate Φ_n by using (C19),

$$\langle \Phi_n | O | \Phi_n \rangle = \sum_{m,k=1}^{15} a_{mn}^* a_{kn} \langle \Psi_m | O | \Psi_k \rangle. \quad (C20)$$

Substituting the results of (C5) to (C18) into (C20) we get the expectation values for the various quantities in the eigenstate

Φ_n ($n = 1, 2, \dots, 15$). In the following expressions Re and Im represent the real and imaginary parts of the bracked quantities, respectively.

$$\begin{aligned} \langle \Phi_n | L_x | \Phi_n \rangle = \text{Re} \left[-\sqrt{2} (a_{1n}^* a_{6n} + a_{2n}^* a_{7n} + a_{3n}^* a_{8n} \right. \\ \left. + a_{4n}^* a_{9n} + a_{5n}^* a_{10n} + a_{6n}^* a_{11n} + a_{7n}^* a_{12n} + a_{8n}^* a_{13n} \right. \\ \left. + a_{9n}^* a_{14n} + a_{10n}^* a_{15n}) \right]. \end{aligned}$$

$$\begin{aligned} \langle \Phi_n | L_y | \Phi_n \rangle = \text{Im} \left[-\sqrt{2} (a_{1n}^* a_{6n} + a_{2n}^* a_{7n} + a_{3n}^* a_{8n} \right. \\ \left. + a_{4n}^* a_{9n} + a_{5n}^* a_{10n} + a_{6n}^* a_{11n} + a_{7n}^* a_{12n} + a_{8n}^* a_{13n} \right. \\ \left. + a_{9n}^* a_{14n} + a_{10n}^* a_{15n}) \right], \end{aligned}$$

$$\langle \Phi_n | L_z | \Phi_n \rangle = -|a_{1n}|^2 - |a_{2n}|^2 - |a_{3n}|^2 - |a_{4n}|^2$$

$$- |a_{5n}|^2 + |a_{11n}|^2 + |a_{12n}|^2 + |a_{13n}|^2 + |a_{14n}|^2 + |a_{15n}|^2,$$

$$\langle \tilde{\Phi}_n | S_x | \tilde{\Phi}_n \rangle = \text{Re} \left[2 (a_{1n}^* a_{2n} + a_{4n}^* a_{5n} + a_{6n}^* a_{7n} + a_{9n}^* a_{10n} + a_{11n}^* a_{12n} + a_{14n}^* a_{15n}) + \sqrt{6} (a_{2n}^* a_{3n} + a_{3n}^* a_{4n} + a_{7n}^* a_{8n} + a_{8n}^* a_{9n} + a_{12n}^* a_{13n} + a_{13n}^* a_{14n}) \right],$$

$$\langle \tilde{\Phi}_n | S_y | \tilde{\Phi}_n \rangle = \text{Im} \left[2 (a_{1n}^* a_{2n} + a_{4n}^* a_{5n} + a_{6n}^* a_{7n} + a_{9n}^* a_{10n} + a_{11n}^* a_{12n} + a_{14n}^* a_{15n}) + \sqrt{6} (a_{2n}^* a_{3n} + a_{3n}^* a_{4n} + a_{7n}^* a_{8n} + a_{8n}^* a_{9n} + a_{12n}^* a_{13n} + a_{13n}^* a_{14n}) \right],$$

$$\langle \tilde{\Phi}_n | S_z | \tilde{\Phi}_n \rangle = 2 (|a_{1n}|^2 + |a_{6n}|^2 + |a_{11n}|^2 - |a_{5n}|^2 - |a_{10n}|^2 - |a_{15n}|^2) + |a_{2n}|^2 + |a_{7n}|^2 + |a_{12n}|^2 - |a_{4n}|^2 - |a_{9n}|^2 - |a_{14n}|^2,$$

$$\begin{aligned} \langle \tilde{\Phi}_n | (h_D)_x | \tilde{\Phi}_n \rangle = & -\frac{2}{7} \text{Re} (a_{1n}^* a_{2n} + a_{4n}^* a_{5n} + a_{11n}^* a_{12n} + a_{14n}^* a_{15n}) - (6\sqrt{2}/7) \text{Re} (a_{1n}^* a_{6n} - a_{5n}^* a_{10n} - a_{6n}^* a_{11n} + a_{10n}^* a_{15n}) + \frac{12}{7} \text{Re} (a_{1n}^* a_{12n} + a_{4n}^* a_{15n}) \\ & - (\sqrt{6}/7) \text{Re} (a_{2n}^* a_{3n} + a_{3n}^* a_{4n} + a_{12n}^* a_{13n} + a_{13n}^* a_{14n}) \\ & - (3\sqrt{2}/7) \text{Re} (a_{2n}^* a_{7n} - a_{4n}^* a_{9n} - a_{7n}^* a_{12n} + a_{9n}^* a_{14n}) \\ & + (6\sqrt{6}/7) \text{Re} (a_{2n}^* a_{13n} + a_{3n}^* a_{14n}) \\ & + \frac{4}{7} \text{Re} (a_{6n}^* a_{7n} + a_{9n}^* a_{10n}) \end{aligned}$$

$$+ (2\sqrt{6}/7) \operatorname{Re} (a_{7n}^* a_{8n} + a_{8n}^* a_{9n}),$$

$$\begin{aligned} \langle \Phi_n | (h_D)_y | \Phi_n \rangle = & -\frac{2}{7} \operatorname{Im} (a_{1n}^* a_{2n} + a_{4n}^* a_{5n} \\ & + a_{11n}^* a_{12n} + a_{14n}^* a_{15n}) - (6\sqrt{2}/7) \operatorname{Im} (a_{1n}^* a_{6n} - a_{5n}^* a_{10n} \\ & - a_{6n}^* a_{11n} + a_{10n}^* a_{15n}) - \frac{12}{7} \operatorname{Im} (a_{1n}^* a_{12n} + a_{4n}^* a_{15n}) \\ & - (\sqrt{6}/7) \operatorname{Im} (a_{2n}^* a_{3n} + a_{3n}^* a_{4n} + a_{12n}^* a_{13n} + a_{13n}^* a_{14n}) \\ & - (3\sqrt{2}/7) \operatorname{Im} (a_{2n}^* a_{7n} - a_{4n}^* a_{9n} - a_{7n}^* a_{12n} + a_{9n}^* a_{14n}) \\ & - (6\sqrt{6}/7) \operatorname{Im} (a_{2n}^* a_{13n} + a_{3n}^* a_{14n}) \\ & + \frac{4}{7} \operatorname{Im} (a_{6n}^* a_{7n} + a_{9n}^* a_{10n}) \\ & + (2\sqrt{6}/7) \operatorname{Im} (a_{7n}^* a_{8n} + a_{8n}^* a_{9n}), \end{aligned}$$

$$\begin{aligned} \langle \Phi_n | h_z | \Phi_n \rangle = & \frac{4}{7} (|a_{1n}|^2 - |a_{5n}|^2 - |a_{7n}|^2 + |a_{9n}|^2 \\ & + |a_{11n}|^2 - |a_{15n}|^2) + \frac{2}{7} (|a_{2n}|^2 - |a_{4n}|^2 + |a_{12n}|^2 \\ & - |a_{14n}|^2) + \frac{8}{7} (-|a_{6n}|^2 + |a_{10n}|^2) - (6\sqrt{2}/7) \\ & \cdot \operatorname{Re} (a_{2n}^* a_{6n} + a_{5n}^* a_{9n} - a_{7n}^* a_{11n} - a_{10n}^* a_{14n}) \\ & - (6\sqrt{3}/7) \operatorname{Re} (a_{3n}^* a_{7n} + a_{4n}^* a_{8n} - a_{8n}^* a_{12n} - a_{9n}^* a_{13n}), \end{aligned}$$

$$\begin{aligned} \langle \Phi_n | v_{11} | \Phi_n \rangle = & -\frac{1}{7} (|a_{1n}|^2 + |a_{2n}|^2 + |a_{3n}|^2 \\ & + |a_{4n}|^2 + |a_{5n}|^2 + |a_{11n}|^2 + |a_{12n}|^2 + |a_{13n}|^2 \\ & + |a_{14n}|^2 + |a_{15n}|^2) + \frac{2}{7} (|a_{6n}|^2 + |a_{7n}|^2 + |a_{8n}|^2 \end{aligned}$$

$$+ |a_{9n}|^2 + |a_{10n}|^2) + \frac{6}{7} \operatorname{Re} (a_{1n}^* a_{11n} + a_{2n}^* a_{12n} + a_{3n}^* a_{13n} \\ + a_{4n}^* a_{14n} + a_{5n}^* a_{15n}),$$

$$\langle \Phi_n | v_{12} | \Phi_n \rangle = - \frac{6}{7} \operatorname{Im} (a_{1n}^* a_{11n} + a_{2n}^* a_{12n} + a_{3n}^* a_{13n} \\ + a_{4n}^* a_{14n} + a_{5n}^* a_{15n}),$$

$$\langle \Phi_n | v_{13} | \Phi_n \rangle = - (3\sqrt{2}/7) \operatorname{Re} (a_{1n}^* a_{6n} + a_{2n}^* a_{7n} + a_{3n}^* a_{8n} \\ + a_{4n}^* a_{9n} + a_{5n}^* a_{10n}) + (3\sqrt{2}/7) \operatorname{Re} (a_{6n}^* a_{11n} + a_{7n}^* a_{12n} \\ + a_{8n}^* a_{13n} + a_{9n}^* a_{14n} + a_{10n}^* a_{15n}),$$

$$\langle \Phi_n | v_{22} | \Phi_n \rangle = - \frac{1}{7} (|a_{1n}|^2 + |a_{2n}|^2 + |a_{3n}|^2 + |a_{4n}|^2 \\ + |a_{5n}|^2 + |a_{11n}|^2 + |a_{12n}|^2 + |a_{13n}|^2 + |a_{14n}|^2 \\ + |a_{15n}|^2) + \frac{2}{7} (|a_{6n}|^2 + |a_{7n}|^2 + |a_{8n}|^2 + |a_{9n}|^2 \\ + |a_{10n}|^2) - \frac{6}{7} \operatorname{Re} (a_{1n}^* a_{11n} + a_{2n}^* a_{12n} + a_{3n}^* a_{13n} + a_{4n}^* a_{14n} \\ + a_{5n}^* a_{15n}),$$

$$\langle \Phi_n | v_{23} | \Phi_n \rangle = - (3\sqrt{2}/7) \operatorname{Im} (a_{1n}^* a_{6n} + a_{2n}^* a_{7n} \\ + a_{3n}^* a_{8n} + a_{4n}^* a_{9n} + a_{5n}^* a_{10n} - a_{6n}^* a_{11n} - a_{7n}^* a_{12n} \\ - a_{8n}^* a_{13n} - a_{9n}^* a_{14n} - a_{10n}^* a_{15n}),$$

$$\langle \Phi_n | v_{33} | \Phi_n \rangle = \frac{2}{7} (|a_{1n}|^2 + |a_{2n}|^2 + |a_{3n}|^2 + |a_{4n}|^2 \\ + |a_{5n}|^2 + |a_{11n}|^2 + |a_{12n}|^2 + |a_{13n}|^2 + |a_{14n}|^2$$

$$+ |a_{15n}|^2) - \frac{4}{7} (|a_{6n}|^2 + |a_{7n}|^2 + |a_{8n}|^2 + |a_{9n}|^2 + |a_{10n}|^2).$$

We now may perform the required statistical average by making an ensemble average of each derived quantities over the 15 eigenstates of the d_e level. This is done by weighting each contribution by the appropriate Boltzmann factor as is discussed in Sec. VII B.

APPENDIX D

A STUDY ON THE QUESTION OF AUGER AFTEREFFECTS
IN HYDRATED COBALTOUS CHLORIDES

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A STUDY ON THE QUESTION OF AUGER AFTEREFFECTS
IN HYDRATED COBALTOUS CHLORIDES

Since we found no evidence of Auger aftereffects for CoO we have also started to study the hydrated cobaltous compounds, $\text{CoCl}_2 \cdot n\text{H}_2\text{O}$ ($n = 0, 2, 4, 6$). Ingalls and DePasquali⁶ reported that they observed two charge states (Fe^{2+} and Fe^{3+}) in the Mössbauer spectra of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. They attributed these multiple charge states to Auger aftereffects. Our systematic variation⁵ of the number of attached water molecules, however, suggests that the broadened spectra may be explained by an alternative mechanism, not requiring the postulation of Auger aftereffects. Our data on these hydrated materials appear to be most easily explained by assuming a metastable lattice rearrangement caused by the local recoil energy accompanying an electron capture and neutrino emission.

The hydrated cobaltous chloride compounds were prepared by forming a $\text{Co}^{57}\text{Cl}_2$ -doped CoCl_2 sample, which was weighed and allowed to pick up water to form $\text{CoCl}_2 \cdot n\text{H}_2\text{O}$. These sources were contained in argon atmospheres in air-tight capsules during Mössbauer runs, thereby keeping water vapor from being absorbed by them. Mössbauer spectra of Fe^{57} in $\text{CoCl}_2 \cdot n\text{H}_2\text{O}$ ($n = 0, 2, 4, 6$) at room temperature are shown in Fig. 29.

Fig. 29

Mössbauer spectra of $\text{CoCl}_2 \cdot n\text{H}_2\text{O}$ ($n = 0, 2, 4, 6$) at 295°K .

FIG. 29

Fig. 30. Temperature dependence of Mössbauer spectra of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.

The Mössbauer doublet spectrum for $n=0$ is as reported earlier⁹. For $n=2, 4, 6$, we again observe simple doublets whose line positions and quadrupole splittings are shown in Table 6(a). The quadrupole splittings for $n=2, 4, 6$ are roughly the same and are almost twice as large as that for $n=0$. There are substantial asymmetries in the Mössbauer doublets at room temperature, and as shown in Fig. 30 and Table 6(b) the asymmetry for $n=6$ decreases with decreasing temperature. These results indicate that the asymmetries result from the anisotropy in the angular dependence of the recoil-free fraction^{51,52}. It should be noted that it is not possible to ascribe an Fe^{3+} doublet⁶ hidden within the peak at about $v=0$, because this would require a substantial broadening of this peak compared to the $v \approx -2$ mm/sec peak, which is not observed. As n is increased from 2 to 6, we observed a resonance pattern which is very similar to the initial $n=2$ pattern, even though the compound where $n=2$ is distinct from that where $n=6$, and the width of both lines increases with increasing n . This result can be understood if we postulate that the recoiling $\text{Fe}^{57\text{m}}$ nucleus, whose recoil energy is of order 3eV when the neutrino accompanying K-capture is emitted, causes a local rearrangement of the lattice resulting in a geometric configuration of ions near the Mössbauer isomer similar to the case where $n=2$. This type of recoil aftereffect is not unreasonable, because the difference in the energy of stability of the two hydrated compounds must be very small, since $n=6$ form converts to the $n=2$ form within 20°C of room temperature, indicating that a very minute energy ($\sim 0.01\text{eV} \ll 3\text{eV}$), is sufficient to convert one form to another.

Table 6. Experimental results for the hydrated cobaltous chlorides.

(a) The results related to Fig. 29.

n	Doublet line positions (mm/sec)		Quadrupole splitting (mm/sec)	Ratio of intensities of doublet
0	-1.57	-0.70	0.87 ± 0.05	0.87 ± 0.06
2	-2.46	-0.20	2.26 ± 0.10	0.69 ± 0.05
4	-2.20	-0.23	1.97 ± 0.10	0.49 ± 0.05
6	-2.07	-0.40	1.67 ± 0.10	0.46 ± 0.05

(b) The results related to $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

Tempera- ture of run ($^{\circ}\text{K}$)	Doublet line positions (mm/sec)		Quadrupole splitting (mm/sec)	Ratio of intensities of doublet
295	-2.07	-0.40	1.67 ± 0.10	0.46 ± 0.05
197	-2.23	-0.34	1.89 ± 0.10	0.51 ± 0.05
77	-2.61	-0.13	2.48 ± 0.10	0.58 ± 0.05