Nucleogenic iron charge states in CoO studied by Mössbauer spectroscopy

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Abstract

Single crystal of CoO was doped by about 40-at. ppm of $^{57}$Co. Mössbauer spectra were measured vs. sample orientation, temperature and under reduced oxygen pressure, i.e., for a low cobalt vacancy concentration. Distinctly different iron charge states coexist till about 866 K. A mixed-valent state is observed above this temperature. It evolves gradually towards the Fe$^{2+}$ state above 1255 K due to the decreasing mobility of holes, as compared to the mobility of the electrons. The ratio of the mobility of holes to the mobility of electrons increases with the increasing vacancy concentration, i.e., with the increasing oxygen pressure. Defects order into clusters below 866 K leaving behind almost perfect structure. A recoilless fraction exhibits some anharmonicity above 923 K.
1 Introduction

Cobaltous oxide Co$_{1-x}$O belongs to Fm3m space group. It is a non-stoichiometric p-type semiconductor with a lattice parameter of 4.26 Å at ambient temperature [1]. Parameter $x$ denotes a concentration of cobalt vacancies and it depends upon temperature and oxygen pressure increasing with the increasing temperature and oxygen pressure both. There are practically no Co interstitials, and the oxygen sub-lattice is almost perfectly ordered. Cobalt d band is located between Co 4s band and the oxygen 2p band. The energy gap between cobalt d band and the cobalt 4s band is 2.8 eV [2]. This is an energy gap between completely filled valence band and the empty conduction band in the ground state.

CoO is a stable phase either in the very high temperatures or in the lower temperatures provided the oxygen pressure is sufficiently low in the latter case. A reduction to the metallic phase requires presence of the reducing atmosphere. The oxide decomposes into liquid metal and gaseous oxygen at the melting temperature. It can be oxidized to Co$_2$O$_3$ mixed valence oxide at lower temperatures and under high oxygen pressure [3]. The latter oxide could be further oxidized to a purely trivalent oxide Co$_3$O$_4$ at high oxygen pressure and lower temperatures than those needed to produce mixed valence oxide. However, kinetics of the latter reaction is extremely slow, and hence it is very difficult to make trivalent oxide by a direct oxidation. There are other oxides of cobalt as well, but they cannot be made by direct oxidation. Both mixed valence and trivalent oxides are unstable at high temperatures decomposing to the formally divalent oxide CoO, the latter being a sole cobalt oxide stable at high temperatures. A trivalent oxide decomposes at much lower temperatures than the mixed valence oxide. Decomposition may lead to a mixed valence oxide provided the temperature is low enough and the oxygen pressure is sufficiently high. Perfectly stoichiometric phase cannot be made, i.e., cobalt vacancies are always present. Vacancies are believed to stay in the uncharged state in the ground state of the crystal. Hence, each vacancy has to be accompanied by two $^{+3}$Co ions in order to maintain charge neutrality. A vacancy can be excited to either singly or doubly negatively charged state converting one or two trivalent cobalt ions into commonly encountered divalent ions, respectively.

Cobaltous oxide has been the subject of several Mössbauer investigations [4-17]. These experiments have shown that $^{57}$Fe exists in both divalent and trivalent high spin states in CoO. Some controversial explanation of the presence of ferric line in CoO spectra has been given. Metastable charge state model [4, 6] was not confirmed by the delayed coincidence technique [7]. It was assumed that nucleogenic $^{3+}$Fe ion is stabilized by some sort of pre-existing lattice defects [7]. A structural model [9-11] suggesting the co-existence of two CoO phases being responsible for two charge states observed in the $^{57}$Co$_{1-x}$O emission spectra was replaced by the competing acceptor model [12, 15]. However, the latter model was in disagreement with the results obtained by the $\gamma$-X-ray coincidence technique [17]. On the other hand, a structural model of two phases is unacceptable, as a second phase was never found by any direct method. This model requires presence of the perfect Fm3m phase as a matrix carrying another phase having the same structure, albeit with each second cation and anion replaced by a vacancy. Ferrous ions are expected to reside in the matrix, while ferric ions have to stay in the dispersed phase. A simple calculation shows that such a structure in the more or less ionic compound is unstable. Ferric iron embedded in this hypothetical phase has to experience some electric quadrupole interaction never observed. It has to be noted that the electric field gradient is generated in such a phase by the nearest neighbor anions, and
hence it is expected to be quite large even for the ferric high spin ion. Another possibility is
that the dispersed phase is composed of some higher oxide, e.g. mixed valence oxide. However, Mössbauer spectra are in disagreement with the above hypothesis. In most experiments a mixed-valent state was observed above \(823 \text{ K} \) \([6, 13, 16]\). Relaxation valence averaging mechanism accounting for the observed effect was proposed \([13, 14]\). However, no evidence for the time dependent effects in the Mössbauer spectra was shown, and hence the last model is again unsupported experimentally hypothesis.

Therefore it seemed essential to re-investigate behavior of the nucleogenic iron in the CoO matrix using as perfect samples as available, and applying clean oxidants. Mixtures of CO/CO\(_2\) used previously \([9-14]\) are not very suitable as one can expect some reactions with carbon at very high temperatures provided the carbon concentration is sufficiently high as in the mixtures above mentioned.

The present paper deals with the emission Mössbauer spectroscopy applied to Co\(_{1-x}\)O single crystal. The main aim of the work was to study the behavior of \(^{57}\text{Fe} \) impurity in cobaltous oxide under reduced oxygen pressure. The model proposed here describes nucleogenic Fe temperature evolution of aliovalent charge states in the wide temperature range studied.

2 Experimental

CoO single crystal plates having 80 µm thickness and \(\langle111\rangle\) direction perpendicular to the surface of dimensions 5 × 4.4 mm have been prepared. The samples were tested for mosaicity and the presence of Co\(_3\)O\(_4\)/Co\(_2\)O\(_3\) phases using electron back-scattering and standard X-ray diffraction methods, respectively. Neither significant mosaicity nor measurable concentration of additional phases was observed.

The Mössbauer \((^{57}\text{Co})\text{CoO} \) source was made by diffusing into the crystal 10 mCi of carrier-free \(^{57}\text{Co} \) leading to ca. 40-at. ppm of radioactive cobalt and iron altogether. The source preparation was performed according to the phase diagram of CoO–Co\(_3\)O\(_4\) system \([3]\). The aqueous solution of carrier-free \(^{57}\text{Co} \) in 0.1 n HCl was deposited evenly on the crystal surface, neutralized with aqueous solution of ammonia, and subsequently dried and oxidized at low temperature to Co\(_3\)O\(_4\). The sample in this state was placed in a Pt boat and slowly heated up to 1123 K at low oxygen pressure and subsequently a diffusion anneal was carried at 1333 K for 3 hours in air followed by a cooling sequence under low oxygen pressure. The annealing was performed in a furnace devoted to Mössbauer measurements. The furnace uniaxial goniometer allowed to rotate the sample \textit{in situ}, i.e., to measure angular dependence of the emitted radiation. The crystal remained uncovered from the top. Mössbauer spectra were measured vs. temperature, oxygen pressure, and sample orientation. Spectra were collected in the temperature range from slightly below room temperature (RT) to 1448 K. Room temperature spectra were measured after having the sample quenched from various elevated temperatures. The temperature was controlled by Pt-Pt(10%Rh) thermocouple and stabilized within 1K accuracy by computer based virtual PID controller. A chemical pump maintained oxygen partial pressure at \(10^{-4}\) atm. In order to have clean oxidant a chemical pump was made of fine partly oxidized copper mesh maintained at elevated temperature, and separated by the vacuum line from the Mössbauer furnace. The hot zone of the Mössbauer furnace was made entirely of alundum, and it contained sample in the Pt-boat and a
thermocouple. The heating element was separated from the sample area by a vacuum tight alundum tube. Hence, clean conditions were assured even at the highest temperatures. Additionally, measurements were performed at high temperatures (HT) under oxidizing atmosphere (air). Mössbauer spectra were measured for the beam outgoing in the [110] plane along various directions. Results obtained for the beam parallel to the ⟨111⟩ direction are reported here. A single line $K_x^{57}\text{Fe(CN)}_6\cdot3\text{H}_2\text{O}$ vibrating absorber in conjunction with Kr-filled proportional detector was used. Mössbauer data were collected using the equipment described in Ref. [18]. Normal and anticoincidence spectra were measured for each Mössbauer spectrum to evaluate background under the resonant line. A typical background contribution was 1.3. It is defined as the ratio of the total area under the Mössbauer line, to the area under the 14.4-keV line.

A Lorentzian approximation was used to fit spectra obtained at RT and below, i.e., magnetically split spectra. Remaining spectra were fitted using transmission integral. Typical values of $\chi^2$ ranged from 0.9 to 1.1, while the MISFIT [19, 20] ranged from 6% to 8%.

3 Results

Typical Mössbauer spectra measured in the vicinity of RT are shown in Fig. 1. Isomer shift systematics was used to identify the valence and spin states of particular spectra components. Typical RT spectrum consists of two singlets corresponding to Fe$^{2+}$ and Fe$^{3+}$, both in high spin configuration, and magnetically split component assigned to Fe$^{2+}$. Cobaltous oxide becomes antiferromagnetic in the vicinity of room temperature. Its Néel temperature is about 291 K [9, 10]. Single lines represent paramagnetic state, while the hyperfine pattern is due to antiferromagnetic state. Divalent Fe couples magnetically to Co ordered spins more easily than trivalent iron. The hyperfine field at the iron nucleus of 6 T at RT was obtained. A content of trivalent iron amounts to approximately 10%.

![Mössbauer spectra of $^{57}\text{Co}\text{CoO}$](image)

**Fig. 1.** Mössbauer spectra of $^{57}\text{Co}\text{CoO}$ obtained in the vicinity of RT.
Spectra measured at elevated temperatures are shown in Fig. 2. Actually, ferrous and ferric lines are present in each spectrum obtained between 325 K and 823 K. Mixed-valent state was observed for spectra measured from 923 K to 1255 K. A reduction to divalent state could be seen from 1273 K. Iron impurity diffusion was not observed due to the low oxygen partial pressure, i.e., low concentration of vacancies. However, a significant diffusive broadening is observed at high temperatures under high oxygen pressure.

**Fig. 2.** Mössbauer spectra of $^{57}$CoCoO plotted vs. temperature.

The temperature dependence of isomer shift, i.e., spectrum shift corrected for a second order Doppler effect is plotted in Fig. 3 and Fig. 4. Isomer shifts are reported here as shifts relative to the shift of metallic iron at RT. The upper and lower curves in Fig. 3 correspond to ferric and ferrous iron states, respectively. The coalescence of these lines can be seen in the vicinity of 866 K. The straight line is due to the mixed-valent state of Fe, while the reduction of the nucleogenic iron at very high temperatures is shown in Fig. 4.

**Fig. 3.** Isomer shift vs. temperature. The point marked by triangle was excluded from fitting procedure.

Relative contributions due to divalent and trivalent iron depend upon the sample history. Generally one can conclude that the trivalent iron content increases provided the sample is quenched from the very high temperature and from the high oxygen pressure environment.
Neither the ground state nor the state of the system equilibrium can be reached at low temperatures, as the mobility of defects is very low at these temperatures. If one assumes that iron is oxidized by the $\text{Co}^{3+}$ ions one can conclude that each $\text{Co}^{3+}$ ion is able to oxidize about 100 lattice sites available to newly born iron for almost stoichiometric samples and about 10 such sites for samples quenched from the high oxygen pressure.

4 Discussion

A proposed band structure of CoO is shown in Fig. 5. A defect band is composed of $\text{Co}^{3+}$ ions, uncharged Co vacancies, singly and doubly charged Co vacancies, and a small admixture of Fe ions being either in the divalent or trivalent state of charge. Uncharged vacancies are able to accept up to two electrons. Trivalent cobalt ions, uncharged vacancies and trivalent iron ions are acceptors, singly charged vacancies can be either acceptors or donors, while doubly charged Co vacancies and divalent iron ions are donors. It has to be noted that trivalent cobalt ions are diamagnetic in the ground ionic state. A $\text{Co}^{3+}$ ion located in the vicinity of the divalent iron acts like a strong oxidant for the latter ion, i.e., the electron is transferred from iron to cobalt and hence, a trivalent cobalt transforms into divalent cobalt, while a divalent iron changes into trivalent iron. The above statement is supported by the absence of isolated divalent iron ions in the mixed valence oxide, where all iron impurities are trivalent. One can consider oxidation to the mixed valence oxide as ordering of the uncharged Co vacancies leading to a normal spinel structure. In such a case parameter $x$ reaches a value of 0.25. Even the most non-stoichiometric CoO has the $x$ parameter in the much lower range. However, vacancies lose mobility at lower temperatures and form some kind of clusters having high vacancy concentration, but still much lower than 0.25. The Fm3m structure is preserved within such clusters, and vacancies do not form any periodic structure proposed earlier [9-11]. The concentration of vacancies within such cluster has to saturate at some rather low level due to the fact that the lattice energy is likely to increase rather than decrease for too high vacancy concentration unless some oxygen is available to fuel oxidation to the mixed valence oxide. It seems that vacancy clusters, having the size depending upon the thermal history, attract trivalent cobalt ions at still lower temperatures leaving behind almost perfect cationic sub-lattice. The above attraction is driven by the demand of the charge neutrality, i.e., trivalent cobalt ions are attracted once the temperature is low enough to de-excite charged vacancies to the neutral vacancies. Clusters upon being formed have to coalesce, as they are much more mobile than the surrounding crystal due to the increased vacancy concentration within them. It seems that such clusters are spatially separated even for the very rapidly cooled samples. They contain very many defect states.
Iron produced by the radioactive decay of $^{57}$Co is distributed randomly within the sample, as the isotopic effects could be neglected. A perturbation due to Fe impurities could be neglected as well provided the overall concentration of iron remains very low. Hence, Fe impurities could be considered as isolated ions within the cobalt sub-lattice. The equilibrium is reached in a short time after the decay leading to the high spin ferrous ion in the case of divalent cobalt oxide. Divalent Fe couples magnetically to the ordered divalent Co magnetic moments at the magnetic transition temperature. On the other hand, iron located in the defect clusters or in the vicinity of them transforms rapidly to the high spin ferric ion. Trivalent iron couples magnetically to the ordered cobalt moments at somewhat lower temperature than the magnetic transition temperature [9, 10]. Ferric line is slightly broader than the ferrous line indicating that ferric ions experience some spurious electric quadrupole interaction due to the lattice and charge distribution distortion caused by defects. However, there is no discernible quadrupole splitting as iron ions are shielded by the nearest neighbor anions, and the anion sub-lattice seems to be distorted very weakly by defects. Electronic states reach equilibrium at much shorter time scale than the time window of the Mössbauer effect. The overall concentration of the acceptor states amounts to $4x$ at low temperatures and therefore a very rapid transition to Fe$^{3+}$ is possible in the vicinity of the defect clusters. A relative concentration of ferric iron is much higher than the concentration of trivalent cobalt and even much in excess of $4x$. Hence, it is likely that Fe is oxidized rapidly to some distance from the defect cluster due to the lattice distortion around the cluster. A coherent tunneling process might be partly responsible for the oxidation at low temperatures, as it is observed that the oxidation range increases with the improving stoichiometry of the crystal. On the other hand, isolated ferrous ion in the perfect lattice seems to be a long-lived metastable state having lifetime extending far beyond the time window of the Mössbauer effect. Such behavior is quite understandable as the electron could be either excited to the conduction band at the expense of quite significant energy or to fill the hole in the valence band. However, holes in the valence band are practically absent at low temperatures, as they have to be created transferring electrons from the valence band to the defect band at the expense of some energy.

Trivalent iron converts to mixed-valent Fe with the increasing temperature $T$ due to the thermally activated electron mobility in the defect band. These electrons must come from the valence band leaving behind holes. On the other hand, the isomer shift of ferrous iron evolves
much slower with the temperature (see the lower curve in Fig. 3). Hence, the activation energy to the defect band has to be lower in the vicinity of the defect cluster than in the perfect lattice, i.e., holes remain attracted to the defect clusters. A conversion of the trivalent iron results in a decrease of Fe$^{3+}$ shift represented by the upper curve plotted in Fig. 3. Mixed-valent state is reached in the vicinity of $T_d = 866$ K, i.e., the so-called cluster decomposition temperature. Holes in the valence band become mobile above this temperature, i.e., the electrons can move more or less freely between trivalent and divalent cobalt ions. Hence, trivalent cobalt ions become de-coupled from vacancy clusters. Divalent iron ions disappear above $T_d$ with the onset of trivalent cobalt mobility. The temperature-induced mobility of Co$^{3+}$ is due to the charge transfer between adjacent cobalt ions and it does not require atomic motion. Trivalent Co ions are distributed more or less evenly within the crystal above temperature $T_d$, leading to the rapid oxidation of any iron, i.e., there are plenty of holes available to relax metastable state of isolated ferrous ion to the thermally equilibrated mixed-valent state. Former ferric iron can interact in a similar fashion with the electrons in the defect band transforming itself to the same mixed-valent state. All these processes proceed on a time scale much shorter than the Mössbauer time window, and hence one sees appropriate averages.

Cluster decomposition temperature could be obtained by fitting the isomer shifts for Fe$^{2+}$ and Fe$^{3+}$, respectively. Both shifts included in Fig. 3 follow the equation:

$$S_k = \varepsilon_k \sqrt{1 - \exp \left( \frac{2 U_k (T - T_d)}{T T_d} \right)} + \langle \varepsilon \rangle \quad \text{for } T \leq T_d \quad \text{and} \quad S_k = \langle \varepsilon \rangle \quad \text{for } T > T_d.$$

Here the symbol $\langle \varepsilon \rangle$ denotes isomer shift in the mixed-valent state, $\varepsilon_k$ stands for the isomer shift in the low temperature limit due to either Fe$^{2+}$ or Fe$^{3+}$ states, respectively. Hence, a relationship $k = 1, 2$ holds. On the other hand, parameters $U_k$ are responsible for the temperature evolution of the respective isomer shifts below $T_d$. Table 1 includes parameters obtained for divalent and trivalent iron shifts, respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fe$^{3+}$</th>
<th>Fe$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_k$ [mm/s]</td>
<td>-0.37(5)</td>
<td>-1.1245(8)</td>
</tr>
<tr>
<td>$\langle \varepsilon \rangle$ [mm/s]</td>
<td></td>
<td>-0.834(1)</td>
</tr>
<tr>
<td>$U_k$ [K]</td>
<td>631(27)</td>
<td>12642(450)</td>
</tr>
<tr>
<td>$T_d$ [K]</td>
<td>866(20)</td>
<td></td>
</tr>
</tbody>
</table>

The equation (1) can be obtained in a straightforward manner applying simple relaxation model [21, 22] to the two possible iron charge states. However, this simplest model has to be modified applying Boltzmann-like scaling to the charge exchange frequencies involved as the two states have vastly different effective energies $U_k$. These differences are caused by the lower excitation energy to a cluster than to the isolated defect as discussed already above. This is an effective relaxation model as in the real system direct electron transfer between ferrous and ferric ions is almost prohibited due to the extreme dilution of iron. The electron
has to go over many intermediate states located in the defect band or valence band. Some transfers via the conduction band are possible as well at high temperatures. Hence, the effective energies cannot be interpreted as the real energy levels within the electronic system.

A temperature dependence of the mixed-valent charge-state at high temperatures is plotted in Fig. 4. Due to the fact that charge transfer is very fast at these elevated temperatures one can define the isomer shift as \( S = p_2 S_2 + p_3 S_3 \), where the symbols \( S_2 \) and \( S_3 \) denote distinctly different isomer shifts of the divalent and trivalent ions, respectively. The symbol \( 0 \leq p_2 \leq 1 \) denotes a probability to find iron in the divalent state, while the symbol \( p_3 = 1 - p_2 \) stands for the probability to find iron in the trivalent state. The equilibrium condition leads to the equation \( p_2 \omega_{23} = p_3 \omega_{32} \), where the symbol \( \omega_{23} > 0 \) stands for the transition rate from the divalent to the trivalent state, while the symbol \( \omega_{32} > 0 \) denotes a transition rate from the trivalent to the divalent state. One can assume that the condition \( \omega_{32} \leq \omega_{23} \) is satisfied in the cobaltous oxide. Therefore one obtains the following relationship for the isomer shift:

\[
S = S_3 + (S_2 - S_3) \frac{\omega_{32}}{\omega_{23} + \omega_{32}}. \tag{2}
\]

On the other hand, transition rates can be expressed as \( \omega_{32} = n_e \nu_e \sigma_e \) and \( \omega_{23} = n_p \nu_p \sigma_p \), where the symbol \( e \) denotes an electron in the defect band, while the symbol \( p \) denotes a hole in the same band. Symbols \( n_e, \nu_e \) and \( \sigma_e \) denote concentration of respective carriers, velocity of them, and cross-section for absorption by the iron ion, respectively. Due to the fact that carriers are highly mobile at these temperatures, it is sufficient to consider solely a defect band as the source of carriers. Other carriers are transferred to the defect band prior to the interaction with the very diluted iron ions. The equilibrium is maintained in the defect band. All of the above parameters are positive. The carrier velocity is likely to be strongly temperature dependent. On the other hand, it can be dependent upon sample stoichiometry as well. Cross-sections are likely to be constant in the system under consideration. Carriers concentrations can be expressed as \( n_p = 4x \left\{ 1 - \frac{1}{2} \exp[-(U/T)] \right\} \) and \( n_e = 2x \exp[-(U/T)] \), where \( U > 0 \) stands for the energy gap between the top of the valence band and the narrow defect band to a good approximation. Finally one obtains:

\[
S = S_3 + (S_2 - S_3) \left[ 1 - \alpha + 2\alpha \exp \left( \frac{U}{T} \right) \right]^{-1}, \tag{3}
\]

where \( \alpha = (\nu_p \sigma_p) / (\nu_e \sigma_e) \) denotes the mobility ratio. One can expand the above expression in a Taylor series around some temperature \( T_0 > 0 \) up to the second order. A polynomial fit applied to the HT data set is shown in Fig. 4. One can assume that for very high temperatures, i.e., for \( T \geq T_0 \) a condition \( U << T \) is satisfied. In such a case sample is quite good conductor and the relationship (3) takes on the following simplified form:

\[
S = S_3 + (S_2 - S_3) (1 + \alpha)^{-1}. \tag{4}
\]

The above equation together with parameters obtained from a polynomial fit can be used to calculate the mobility ratio vs. temperature. A comparison with mobility ratio obtained for
high oxygen pressure (air) was made. Resulting curves are plotted in Fig. 6. Holes are more mobile in comparison with electrons for high oxygen pressure, where the high concentration of vacancies leads to enhanced scattering of electrons, and therefore somewhat reduced electron mobility.

Fig. 6. Mobility ratio vs. temperature for high and low oxygen pressures.

One can observe a jump in the isomer shift towards trivalent iron at the onset of the vacancy mobility, the latter leading to evaporation of the vacancy clusters. Such a result is consistent with the model described by the equation (4) as once vacancies become mobile even traces of the coherence are lost leading to the enhancement in the electron scattering. The process occurs within a narrow temperature region suggesting that vacancy clusters contain very many defects each.

A temperature dependence of the recoilless fraction $f$ is shown in Fig. 7. A recoilless fraction at each temperature has been scaled by the value of the recoilless fraction $f_0$ obtained at 325 K. One can define effective mean-squared displacement (MSD) relative to the mean-squared displacement at 325 K as

\[ (-1/q^2) \ln(f/f_0) = a(T - T_N) + b \eta(T - T_a)(T - T_a)^2. \]

Here the symbol $q$ denotes the wave number of the Mössbauer radiation having 14.4-keV energy (7.3 Å$^{-1}$), and $T_N = 325$ K. Linear part of the above curve can be used to evaluate an effective Mössbauer characteristic temperature according to the following equation:

\[ \theta_M = \frac{3h^2}{k_Bma}, \]

where $k_B$ is the Boltzmann’s constant, $h$ stands for the Planck’s constant divided by $2\pi$, and $m$ is the mass of the Mössbauer atom. A temperature $\theta_M$ equals 440(11) K and stays in quite good agreement with the value obtained in Refs. [9, 10]. The anharmonicity parameter $b$
equals $5.7(2) \times 10^{-8}$ Å$^2$ K$^{-2}$. A temperature $T_d$ has been taken as 923 K, while the symbol $\eta(T - T_d)$ denotes the Heaviside function. One has to note that in the high temperature limit ($T > T_d$) the following expression approximates quite well mean-squared displacement $AT + BT^3$ [23-27]. The above expression can be expanded around temperature $T_d$ to the second order leading to the high temperature limit of the equation (5) provided $B = \frac{b}{(3T_d)}$. The latter parameter equals $2.06(7) \times 10^{-11}$ Å$^2$K$^{-3}$. The above high temperature limit of the equation (5) is accurate to the constant $aT_N$. One has to note that vacancy clusters dissolve at temperature well above the onset of anharmonicity. Such behavior is understandable as in order to dissolve a vacancy cluster vacancies have to be mobile. Anharmonic forces are essential to make atoms mobile, and hence to start diffusion of vacancies. Due to the absence of the hyperfine splitting and relatively large acceptance angle of the detector we were neither able confirm nor to reject presence of any quartic terms in the recoilless fraction [23].

![Fig. 7. Effective MSD plotted vs. temperature.](image)

**5 Conclusions**

It has been found that below 1255 K vacancies tend to cluster attracting trivalent cobalt ions below 866 K. Iron atoms either embedded in such clusters or being located in the vicinity of the above mentioned extended defects oxidize to the trivalent high spin state. Remaining iron atoms are located in the almost perfect structure and they stay in the ferrous high spin-state. Activation energies of these two iron states are vastly different as the former one can interact directly with the defects, while the latter one has to release the electron to the conduction band or to absorb a hole from the valence band.

Trivalent cobalt ions become mobile above 866 K due to the charge transfer. The last phenomenon leads to the mixed-valent state of iron. Furthermore, vacancy clusters dissolve at about 1255 K and the vacancies become mobile. Rapid equilibration of the vacancy concentration governed by the oxygen pressure is achieved above this temperature. Furthermore, all higher oxides disappear rapidly in this temperature range. It seems that there is an upper limit on the defect cluster size due to the increasing energy of the lattice deformation. Hence, there is no phase separation into sub-phases characterized by the almost perfect lattice and rich in defects. There is an upper limit on the defect concentration within a cluster due to the increasing lattice deformation energy with the increasing defect concentration. However, defect clustering is energetically favored at low defect concentrations. Due to these limitations defects do not form periodic structures. One can roughly estimate that the maximum concentration of defects within clusters stays much more
below a corresponding defect concentration in isostructural FeO, where even for the most stoichiometric ferrous oxide the anion lattice is disturbed to such an extend, that a discernible quadrupole interaction is easily seen. We have observed a development of the significant mosaic of the single crystal at high oxygen pressure and in the temperature region, where vacancies become mobile. Such behavior has been observed while looking upon directional dependence of the diffusional broadening. These facts allow to conclude that defects become inhomogeneously distributed while lowering temperature.

The hypothesis on clustering of the acceptor defects is supported by the non-linearity between amount of trivalent iron seen in comparison with the overall concentration of the intrinsic acceptor-type defects. One sees a jump of the isomer shift towards trivalent iron on the onset of the vacancy mobility. This is an indication that clusters contain many defects each.

The ratio of holes to electrons mobilities decreases with the increasing temperature and it depends strongly upon defect concentration. Electrons loose the mobility in comparison to holes with the increased defect concentration, and gain mobility with the increasing temperature at very high temperatures. The latter behavior indicates that CoO remains as semiconductor even at very high temperatures.

Vibrational dynamics of the iron impurity remains harmonic till about 923 K, i.e., the anharmonicity appears well below the onset of the vacancy mobility. The onset of anharmonicity is clearly seen at higher temperatures. Recoilless fractions seem to be similar for both charge states of iron at all temperatures. This is another indication that two phase model [9-11] is inadequate, as it is impossible to maintain the same recoilless fraction having half of the adjacent anions removed.

All after-effects caused by the radioactive decay vanish at a time scale short compared to the Mössbauer time window. However, a divalent state of iron has to be considered as a long-lived metastable state at low temperatures. There are always many trivalent cobalt ions ready to oxidize newly born iron, but they are unreachable for iron born in the almost perfect environment, at least within a time window accessible to the Mössbauer effect. Highly ionized states of iron occurring immediately after the nuclear decay seem to relax due to the rapid transfer of electrons from the adjacent neighborhood, as distant defects have no influence on the state of iron seen by the emission Mössbauer spectroscopy. A different behavior is seen in insulators almost devoid of the intrinsic defects, where long-lived metastable states of the local origin can be formed for some particular lattice positions and survive beyond the time window of the Mössbauer effect at low temperatures [18].

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