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ANOMALOUS LINE SHAPES OF Fe\textsuperscript{3+}-MÖSSBAUER SPECTRA IN MAGNETICALLY ORDERED SYSTEMS — EFFECTS OF HEAT TREATMENT IMPURITY IONS AND Fe\textsuperscript{3+} ION-CONCENTRATION

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The problem of anomalous Mössbauer line shapes have been studied earlier both experimentally [1-3] and theoretically [4-6]. In the present work study has been made regarding the line shapes of Fe\textsuperscript{3+}-Mössbauer spectra in magnetically ordered Cr\textsubscript{2}O\textsubscript{3}-Fe\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3}-Fe\textsubscript{2}O\textsubscript{3} systems. It is seen that the appearance of anomalous line shapes in these solid solutions is a consequence of their incomplete annealing. This incomplete annealing arises when either the annealing temperature, \( T_{\text{anneal}} \), is low or the annealing time, \( t_{\text{anneal}} \), is short. Figure 1 shows a few representative Mössbauer spectra of the (1-x)Cr\textsubscript{2}O\textsubscript{3} - x Fe\textsubscript{2}O\textsubscript{3} system (x = 3.85, wt.%) annealed at 1250 °C in air for a period of 2 hours before being slow-cooled to room temperature. These spectra clearly show the presence of anomalous line shapes which are characterised by the enhancement in the intensity of their central portions. Annealing the Cr\textsubscript{2}O\textsubscript{3}-3.85 wt. % Fe\textsubscript{2}O\textsubscript{3} system at 1400 °C in air for a period of 10 hours has been found to make this anomalous central enhancement disappear. This has been seen to be true whether the sample is quenched or slow-cooled from 1400 °C.

Figure 2 shows Mössbauer spectra of the sample quenched from 1400 °C. We see only normal Mössbauer spectra with no indication of any central enhancement. Similar results have been obtained in the Al\textsubscript{2}O\textsubscript{3}-29 mol. % Fe\textsubscript{2}O\textsubscript{3} system also which when annealed at 1350 °C for 10 hours in air, before being slow-cooled, has been found to give rise to the anomalous Mössbauer line shapes. Increasing the annealing temperature to 1500 °C has been found to make the anomalous central enhancement disappear. This shows that this phenomenon of heat treatment-dependence of Mössbauer line shapes is general in nature and is not specific to any particular solid solution. In order to have a better understanding of this phenomenon, extensive Mössbauer measurements have been made on the (1 - x)Cr\textsubscript{2}O\textsubscript{3} - x Fe\textsubscript{2}O\textsubscript{3} system (x ≤ 7.41 wt.%) at various temperatures between 80 and 300 K. About two hundred and fifty Mössbauer spectra of the Cr\textsubscript{2}O\textsubscript{3}-Fe\textsubscript{2}O\textsubscript{3} solid solutions have been recorded after subjecting them to various heat treatments, after varying Fe\textsubscript{2}O\textsubscript{3} concentration in them, after subjecting them to pressure before annealing and
after doping some of the solid solutions with nonmagnetic and magnetic impurity ions. For making these extensive studies, following samples were prepared:

(1) Samples of category A, with $x = 3.85$ wt. %, were annealed in air at $1400 \, ^\circ\text{C}$ for a period of 2, 4, 6 and 10 hours before cooling them slowly to room temperature.

(2) The sample of category B ($x = 3.85$ wt. %) was annealed in air at $1400 \, ^\circ\text{C}$ for 10 hours and then quenched in water to room temperature.

(3) Samples of category C, $x = 3.85$ wt. %, were annealed in air at $1250 \, ^\circ\text{C}$ for a period of 2, 9, 10, 26 and 60 hours and then cooled slowly to room temperature.

(4) Samples of category D, $x = 3.85$ wt. %, were subjected to a pressure of 1 t psi ($t_{\text{ann}} = 3, 10, 17$ hours), 2 t psi ($t_{\text{ann}} = 60$ hours) and 3.75 t psi ($t_{\text{ann}} = 10$ hours) respectively before being annealed in air at $1250 \, ^\circ\text{C}$ (t psi = ton per square inch). These samples were slow-cooled to room temperature after annealing.

(5) Samples of category E contained various concentrations of $\text{Fe}^{3+}$ ions ($x = 1.77, 3.85, 5.66$ and 7.41 wt. %) and were annealed in air at $1250 \, ^\circ\text{C}$ for 10 hours before slow-cooled to room temperature.

(6) Samples of category F contained nonmagnetic and magnetic impurity ions, $\text{Al}^{3+}$, $\text{Gd}^{3+}$, $\text{Fe}^{2+}$ and $\text{Ni}^{2+}$, doped in various concentrations in $\text{Cr}_2\text{O}_3 - 3.85$ wt. % $\text{Fe}_2\text{O}_3$ system in the form of $\text{Al}_2\text{O}_3$, $\text{Gd}_2\text{O}_3$, $\text{FeTiO}_3$ and $\text{NiTiO}_3$ respectively. In the samples containing $\text{Al}^{3+}$ and $\text{Fe}^{2+}$ impurity ions, the ratio of the concentrations of impurity ions and $\text{Fe}^{2+}$ ions, $X_{\text{imp}}/X_{\text{Fe}^{3+}}$, was 0.5. The samples containing $\text{Gd}^{3+}$ had

$$X_{\text{imp}}/X_{\text{Fe}^{3+}} = 0.25 \text{ and } 0.5$$
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whereas for the Ni\(^{2+}\) doped samples \(X_{\text{imp}}/X_{\text{Fe}^{3+}}\) was 0.5, 2.0 and 7.0. All these samples were fired in air, except the Fe\(^{2+}\)-doped one which was annealed in vacuum, at 1 250 °C for 10 hours and then were slow-cooled to room temperature.

(7) Similar to the case of Al\(_2\)O\(_3\)-Fe\(_2\)O\(_3\) system [7], vacuum-annealing is expected to create Fe\(^{2+}\) ions in the Cr\(_2\)O\(_3\)-Fe\(_2\)O\(_3\) system also. In order to see the effect of these Fe\(^{3+}\) ions, if produced, on the Fe\(^{3+}\) Mossbauer line shapes, sample of category G was prepared by annealing the (1 - \(x\)) Cr\(_2\)O\(_3\) - \(x\)Fe\(_2\)O\(_3\) mixture (\(x = 3.85\) wt.%) in vacuum at 1 250 °C for 10 hours and then cooling it slowly to room temperature. For a better understanding of the results obtained in this sample, more samples were prepared. Sample of category H, \(x = 3.85\) wt.%, was first annealed in vacuum for 10 hours and then was refired in air for the next 10 hours. The sample of category I (\(x = 3.85\) wt.%) was annealed in vacuum for 20 hours whereas the sample of category J was just \(x\)-Fe\(_2\)O\(_3\) annealed in vacuum for 10 hours. All these samples (belonging to categories H, I, J) were annealed at 1 250 °C and were slow-cooled to room temperature.

The results obtained are summarised in figure 3 where the temperature interval \(T_N - T^*\), during which the anomalous line shapes are observed, is plotted as a function of annealing time, concentration of impurity ions, \(X_{\text{imp}}\), and the Fe\(^{3+}\) ion-concentration, \(x\). We see an exponential decrease in \(T_N - T^*\) with increasing \(t_{\text{ann}}\) (Fig. 3a). \(T_N = \text{Néel temperature}\). Increasing the annealing temperature or quenching the sample after annealing or subjecting it to high pressure before annealing has also been found to decrease \(T_N - T^*\). However, the effect of \(t_{\text{ann}}\) has been found to be more pronounced than the effects of \(t_{\text{ann}}\) rate of cooling and applied pressure. An annealing for even 2 hours at 1 400 °C has been seen to be enough to make \(T_N - T^* \approx 0\). As seen in figure 3b, c, the effect of both the increasing \(X_{\text{imp}}\) and the increasing \(x\) is to increase \(T_N - T^*\). For all these samples, the Néel temperature, \(T_N\) have been determined by the stationary absorber technique [8]. The definition of the temperature \(T^*\) is a bit arbitrary. We have taken it as the temperature at which the enhancement in the intensity of the central portion of Mossbauer spectrum starts becoming somewhat evident when the temperature is increased towards \(T_N\). More specifically, we have taken \(T^*\) as the temperature where \(I_1/I_0 = 1.76\); here \(I_0\) is the average amplitude of the central peaks and \(I_1\) is the average amplitude of the outermost peaks in the Mossbauer spectrum.

The vacuum-annealed Cr\(_2\)O\(_3\)-3.85 wt. % Fe\(_2\)O\(_3\) solid solution (category G) and the Fe\(^{2+}\)-doped sample (category F), which was also annealed in vacuum, have been found to show identical Mossbauer spectra. They do not show any six-line or anomalous Mossbauer pattern, instead they show a quadrupole doublet, with an isomer shift and splitting characteristic to the Fe\(^{2+}\) compounds, at 80 K which is seen to merge into a broad single line at room temperature (Fig. 4a). An interesting observation is that when the vacuum-annealed Cr\(_2\)O\(_3\)-3.85 wt. % Fe\(_2\)O\(_3\) system (category G) is reannealed, for the next 10 hours, in air at 1 250 °C (category H), anomalous Mossbauer spectra are observed again (Fig. 4b). This reappearance of the anomalous line shapes is not due to any prolonged annealing since the Mossbauer spectra of the sample of category I, where \(t_{\text{ann}} = 20\) hours, have

![Figure 3](image-url)

**FIG. 3.** — Variation of the temperature interval \(T_N - T^*\), during which the anomalous Mossbauer line shapes are observed, in the (1 - \(x\)) Cr\(_2\)O\(_3\) - \(x\)Fe\(_2\)O\(_3\) system with (a) the annealing time \(t_{\text{ann}}\) (\(x = 3.85\) wt.%, category C), (b) the ratio of the concentrations of impurity ions and Fe\(^{3+}\) ions, \(X_{\text{imp}}/X_{\text{Fe}^{3+}}\), in the impurity-doped samples (\(x = 3.85\) wt.%, \(t_{\text{ann}} = 10\) hours, category F) and (c) the concentration, \(x\), of Fe\(^{3+}\) ions (\(t_{\text{ann}} = 10\) hours, category E). All the samples have been annealed in air at 1 250 °C and then cooled slowly to room temperature \((T_N = \text{Néel temperature})\).
It has been shown in some cases [10-15] that an incomplete annealing of the host-impurity system produces a nonuniform distribution of the ions of the diffusing species in the host lattice. Such an inhomogeneous diffusion of the impurity ions causes clustering of these ions in the matrix of the host. These impurity ion-clusters are superparamagnetic [10] and therefore their direction of magnetisation fluctuates randomly with a flip-time given by [6]

$$\tau_F = \tau_0 \exp(KV''/kT),$$

where $n \sim 1$ ($k = \text{Boltzmann’s constant, } K = \text{anisotropy energy constant and } V = \text{volume of the cluster}$). These superparamagnetic clusters give rise to a six-line or an anomalous or a single line Mössbauer pattern depending upon whether $\tau_F > \tau_L$ or $\tau_F < \tau_L$ or $\tau_F \sim \tau_L$ which, at any temperature, is essentially decided by the volume of the cluster; evidently, bigger the cluster-size, larger is the value of $\tau_F$ ($\tau_L = \text{Nuclear Larmor precession time}$).

It is quite likely that in the presently studied $\text{Cr}_2\text{O}_3-\text{Fe}_2\text{O}_3$ solid solutions also, superparamagnetic $\text{Fe}^{3+}$ ion-clustering is taking place when the solid solutions are annealed at $1250^\circ\text{C}$ for short annealing times. Assuming this to be the case, $\tau_F$ has been deduced by comparing the observed line shapes with the theoretically computed ones [9, 16-17]. This gives us $\tau_F$ as a function of $t_{\text{anneal}}$, $x$ and $x_{\text{def}}$. Now from eq. (1) and assuming that $\tau_0$ and $K$ do not depend on the cluster-volume, we get the ratio $V_2/V_1$ as:

$$V_2/V_1 = 1 + C[\ln(\tau_F^{\text{def}}/\tau_F)],$$

where $C = kT/KV^*_1 \sim 1$ for $\tau_F \sim \tau_L$. The dependence of $V_2/V_1$ on $t_{\text{anneal}}$, $x$ and $x_{\text{def}}$ are shown in figure 5; here $V_1$ is the normalising average $\text{Fe}^{3+}$ cluster-volume defined suitably in figure caption for each case. We see an increase in the $\text{Fe}^{3+}$ cluster-volume with increasing $t_{\text{anneal}}$ (Fig. 5a). It is possible to understand this result on the basis of the above mentioned superparamagnetic $\text{Fe}^{3+}$ ion-clustering hypothesis. Annealing the solid solutions for a longer time is expected to diffuse the $\text{Fe}^{3+}$ ions more uniformly in the host matrix. This homogeneous diffusion increases the distance between the $\text{Fe}^{3+}$ ions resulting in an increase in the volume of the $\text{Fe}^{3+}$ ion-clusters. As the effect of increasing the $T_{\text{anneal}}$ or quenching the sample or subjecting it to pressure before annealing is to decrease $T_N - T^*$, it follows that these treatments also give rise to a more homogeneous diffusion of the $\text{Fe}^{3+}$ ions in the host lattice. Similarly the decrease observed in the average $\text{Fe}^{3+}$ cluster-volume with increasing $x$ and $x_{\text{def}}$ (Fig. 5b, c) indicates that the presence of $\text{Fe}^{3+}$ ions in large concentration or those of the impurity ions causes a more nonuniform distribution of the $\text{Fe}^{3+}$ ions in the matrix of the host. This is physically understandable since the solubility of the ions of the diffusing species in the host matrix, at any temperature,
is inversely proportional to the concentration of these ions [18]. Noticing that an increase in the Fe$^{3+}$ cluster-volume means a decrease in the concentration of Fe$^{3+}$ ions at any point $q$ and using the simple diffusion equation [18, 19],
\[
x(q, t) = \frac{x_0}{\sqrt{\pi D t}} e^{-q^2/4Dt},
\]
where $D$ is the diffusion coefficient, $x_0$ is the initial concentration of the Fe$^{3+}$ ions at $q = 0$, $t = 0$ and $t \equiv t_{\text{ann}}$ we have obtained $q^2/4D$ as a function of $t_{\text{ann}}$ [17]. We see an increase in $q^2/4D$ with increasing annealing time. This dependence of $D$ on $t_{\text{ann}}$ at any point $q$, is probably due to the fact that $D$ is expected to depend on the concentration of Fe$^{3+}$ ions [18, 19] which changes at the point $q$ when $t_{\text{ann}}$ changes owing to a change in the volume over which the Fe$^{3+}$ ions are distributed. For evaluating $D$, it is therefore necessary to take this effect into account. Such a calculation is being done [17].

We will now examine the possibility of the presence of electronic relaxation effects in the 1 250 °C-annealed samples in which the anomalous line shapes have been observed. The existence of nonuniformly distributed Fe$^{3+}$ ions and those of the various types of lattice defects, both of which are almost absent in the 1 400 °C-annealed samples as they have been annealed out in them, creates a kind of magnetic disorder in the lattice of these 1 250 °C-annealed solid solutions. This magnetic disorder is expected to highly damp the long-range collective motions of the ionic spins existing in a normal magnetically ordered system [20]. Such a damping of collective modes greatly affects the electronic relaxation mechanisms operative in the system and the system effectively starts behaving like a paramagnetic one as far as the relaxation processes are concerned. This phenomenon can make the electronic relaxation time, $\tau_{\text{relax}} \sim \tau_{\text{rel}}$, giving rise to the anomalous Mössbauer line shapes. It may be mentioned here that the Néel temperature $T_N$, the $T/JT_N$ dependence of the hyperfine field and the temperature dependence of the magnetic structure of the samples of categories A and B, which show normal Mössbauer spectra, have been found to be exactly identical with the corresponding quantities of the samples of category C where anomalous line shapes have been seen. This results puts some doubt on the presence of magnetic disorder and hence on the existence of electronic relaxation effects in the 1 250 °C-annealed samples. However, to understand this result on the basis of superparamagnetic effects is also somewhat difficult and thus it is not possible to predict conclusively whether the observed anomalous spectra are due to superparamagnetic effects or the electronic relaxation effects [17].

The results of the vacuum-annealed samples (Fig. 4) can be understood either by assuming the formation of FeCr$_2$O$_4$, embedded in the Cr$_2$O$_3$ host, upon
vacuum-annealing [21] or by visualising the presence of randomly fluctuating electric field gradient owing to the random jump of vacancies (lattice defects) in the vacuum-annealed samples [22]. Further measurements are being carried out for understanding these results [17].

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