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MÖSSBAUER EFFECT STUDIES OF BERYL

D. C. PRICE, E. R. VANCE, G. SMITH, A. EDGAR and B. L. DICKSON (*)

Department of Solid State Physics, The Australian National University, Canberra, Australia

Abstract. — The $^{57}$Fe Mössbauer spectra of a number of natural beryl (Be$_3$Al$_2$Si$_6$O$_{18}$) crystals indicate the presence of two independent Fe$^{2+}$ sites and one Fe$^{3+}$ site. Measurements of the temperature dependence of the absorption areas indicate that the two Fe$^{2+}$ sites observed are substitutional, and from single crystal studies it appears that one of these is the octahedral Al$^{3+}$ site and the other a tetrahedral site (Be$^{3+}$ or Si$^{4+}$). The Fe$^{3+}$ absorption spectrum was not inconsistent with these ions occupying the Al$^{3+}$ site as had been previously suggested by EPR measurements. Evidence for a heat-induced reduction of Fe$^{3+}$ to Fe$^{2+}$ was obtained. In contrast to previous assignments, the intensities of optical and Mössbauer absorption peaks in various samples indicated a possible association between the absorbance of 810 nm $\sigma$ polarized Fe$^{2+}$ in the octahedral site and of the $\pi$-polarized bands at 810 nm and 1 000 nm with Fe$^{2+}$ in the tetrahedral site.

(*) Present address : Division of Mineral Physics, C.S.I.R.O. North Ryde, N. S. W., 2113, Australia.
and in interstitial sites within the structural channels. Weak, fairly sharp bands at \( \sim 400 \) nm have been attributed to spin-forbidden transitions of Fe\(^{3+}\).

Dvir and Low [4] observed the paramagnetic resonance of Fe\(^{3+}\) in beryl and interpreted their results assuming that most of these ions occupied Al\(^{3+}\) sites.

We believe that the present paper contains the first report of \(^{57}\)Fe Mössbauer measurements made on beryl. The object is to study the locations of the iron ions in the beryl lattice and, subsequently, to examine the above assignments for the optical absorption features.

2. Experimental. — More than a dozen samples of gem-quality, or near gem-quality, natural beryls were studied. Most were of unknown origin and ranged from colourless (goshenite), pink (morganite) to golden, yellow, green and blue (aquamarine). Mössbauer spectra of powders and/or single crystal slices as absorbers were recorded using constant acceleration spectrometers [5] and sources of either \(^{57}\)CoPd or \(^{57}\)CoRh. Absorber thicknesses were usually about \(1/\mu\), where \(\mu\) (\(\sim 15 \) cm\(^{-1}\)) is the non-resonant absorption coefficient for 14.4 keV photons in beryl.

The sources were at room temperature and the spectrometers were calibrated using iron foil absorbers (at room temperature) and the data of Violet and Pipkorn [6].

In some cases samples were heated to examine the effect of this treatment on their Mössbauer spectrum. When this was done the spectra before and after heat treatment were recorded consecutively and all reasonable precautions were taken to ensure that the experimental geometry was unchanged.

Polarized optical absorption spectra were recorded with a Cary 17 spectrophotometer.

EPR spectra were measured with a Varian E12 35 GHz spectrometer using a TE\(_{011}\) cavity. The effect of heat treatment on absorption intensity was determined by mounting a standard sample of V\(^{2+}\) : MgO adjacent to the beryl sample and measuring the absorption relative to that of the standard.

3. Results. — 3.1 Observation of Fe\(^{2+}\). — Figure 2 shows the Mössbauer spectra of a blue beryl at 4.2 K in zero applied magnetic field. The dominant features, which were observed in all of the beryls (in which there was sufficient iron to register discernible absorption peaks) are two pairs of sharp peaks which we associate with Fe\(^{2+}\) in two different sites in the lattice. We shall refer to the outer peaks as arising from Fe\(^{2+}\) in the major site since in all but one of the samples studied this spectrum was more intense than that arising from the other (minor) Fe\(^{2+}\) site.

Typical values of the quadrupole splitting and isomer shift for Fe\(^{2+}\) in the two sites are given in table I. The solid line through the powder spectrum in figure 2a represents the best least-squares fit to the data by two pairs of lorentzian peaks of equal width and area. The major site peaks in all samples were very narrow (\(\sim 0.21 \) mm/s) at 4.2 K, indicating a particularly well-characterized site.

3.2 Observation of Fe\(^{3+}\). — The fit to the spectrum of figure 2a gives no evidence, apart from a slight mis-fit near zero velocity, for any absorption that can be attributed to Fe\(^{3+}\) in the lattice. However, both EPR and optical spectra indicated that ferric iron was almost always present. Its observation in Mössbauer spectra is shown in figure 3, which gives the spectra of a green beryl both in zero applied field and in a field of 6 T applied parallel to the crystal \(c\) axis and perpendicular to the \(\gamma\)-ray direction. The line spectra in the middle of the diagram indicate the positions and relative intensities of the peaks of the Fe\(^{3+}\) major site spectrum (to which we will refer later) while those at the top of the figure indicate the sharp Fe\(^{3+}\) absorption peaks. This sample had only a weak Fe\(^{2+}\) minor site spectrum. On a wider velocity scale, six narrow Fe\(^{3+}\) peaks can be observed. They indicate an effective magnetic field at the \(^{57}\)Fe nucleus of \(\sim 51.5 \) T, and isomer shift and quadrupole splitting values as given in table I. The relative positions and intensities of these Fe\(^{3+}\) peaks are consistent with
FIG. 3. — Mössbauer spectra of a single crystal of a green beryl at 4.2 K with crystallographic c axis perpendicular to the γ-ray direction, both in zero applied field (lower) and in a magnetic field of 6 T applied parallel to the c axis (upper). The source was $^{57}$CoRh at room temperature. The line spectra in the centre of the diagram show the peak positions and relative intensities of the major site Fe$^{2+}$ spectrum in zero applied field (lower) and in the 6T applied field (upper). The line spectrum at the top of the diagram shows the positions and relative intensities of the Fe$^{3+}$ absorption peaks in the applied field spectrum. Note that the Fe$^{3+}$ peak at maximum positive velocity is out of the range of the diagram.

TABLE I

<table>
<thead>
<tr>
<th>Site</th>
<th>Isomer shift (mm/s)</th>
<th>Quadrupole splitting (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{2+}$ (major site)</td>
<td>1.3</td>
<td>2.7</td>
</tr>
<tr>
<td>Fe$^{2+}$ (minor site)</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>~0.6</td>
<td>~0.7</td>
</tr>
</tbody>
</table>

Isomer shifts measured relative to an iron foil absorber. All figures represent measurements at 4.2 K.

$^{57}$Fe$^{3+}$ nuclei experiencing an electric field gradient that is axially symmetric about the magnetic field direction (the crystal c axis). This result agrees with the assignment of Dvir and Low [4], that is, that the Fe$^{3+}$ is predominantly in Al$^{3+}$ sites.

As the applied field was decreased from 6 T, peaks corresponding to the $m_s = -\frac{3}{2}$ state of Fe$^{2+}$ were observed, and at lower fields all the lines broadened until, in zero field, they were almost undetectable. It would appear that this is due to rapid spin-spin relaxation of the Fe$^{3+}$ ions among the various states of the $^5S$ ground multiplet. It one sample, which optical and EPR measurements indicated contained appreciably more Fe$^{3+}$ than others studied, small relatively sharp peaks were detectable in the Mössbauer spectrum in zero applied field at approximately 0.2 mm/s and 1.0 mm/s (i.e. roughly where peaks should be expected in the limit of very fast relaxation), indicating that the Fe$^{3+}$ relaxation was faster in this than in other samples. In no sample that we studied was the Fe$^{3+}$ concentration such that well-resolved paramagnetic hyperfine structure was observable in zero applied field.

3.3 LATTICE LOCATION OF THE Fe$^{2+}$ IONS. — While the isomer shifts and quadrupole splittings of the spectra of Fe$^{2+}$ in the major and minor sites (Table I) are indicative of octahedral and tetrahedral coordination respectively [7], more detailed evidence of their location in the beryl lattice was sought. In an attempt to distinguish the sites as being substitutional or interstitial, measurements of the temperature dependence of the relative areas of the spectra were made using the blue beryl absorber for which 4.2 K spectra are shown in figure 2. The results of these measurements are shown in figure 4. The solid lines were calculated assuming a Debye model for the vibrations of the Fe$^{2+}$ ion, and are labelled with the effective Debye temperatures (of the Fe$^{2+}$ ion) to which they correspond. From these we might conclude that the Debye temperatures for Fe$^{2+}$ in the major and minor sites are of the order of 500 K and 300 K respectively. It might be expected that the most likely interstitial sites for Fe$^{2+}$ ions would be either in the structural channels (with highest point symmetry $C_{6v}$), between two Be$^{2+}$ ions (point symmetry $C_{3v}$) or between two Al$^{3+}$ ions (point symmetry $C_{3v}$) [8]. Since these sites are all relatively large and open, we take the results of figure 4 to indicate that the Fe$^{2+}$ observed is in substitutional sites.

FIG. 4. — Temperature dependence of the relative areas of the Fe$^{2+}$ major site and minor site Mössbauer spectra of the blue beryl whose 4.2 K spectra are shown in figure 2. The solid lines are calculated from the Debye model with the characteristic temperatures indicated.
In the absence of an externally imposed quantization direction there are only three inequivalent cation sites in the beryl unit cell into which the iron impurities may substitute. These sites, their point symmetry and the approximate radius [9] of the ion that normally occupies them are given in table II. All cations are coordinated to oxygen ions only. The approximate radii of an Fe\textsuperscript{2+} ion when coordinated octahedrally and tetrahedrally to oxygen ions are 0.77 Å and 0.63 Å respectively [9].

Mössbauer measurements were made on single crystals of several beryls in an attempt to determine the symmetry of the electric field gradient (e. f. g.) at the \textsuperscript{57}Fe\textsuperscript{2+} nuclei in the major and minor sites. The e. f. g. symmetry is, obviously, related to the Fe\textsuperscript{2+} site symmetry but is not necessarily identical to it. Its symmetry cannot be lower than that of the site but it may be higher: the e. f. g. must always have three mirror planes, and in some cases ions that reduce the site symmetry may not measurably reduce the e. f. g. symmetry. The last column of table II, lists one of the symmetry elements of the point group of each cation site. In view of the above considerations these symmetry elements imply that at each cation site one of the e. f. g. principal axes must be parallel to the crystal c axis. We ignore, for the moment, the possibility that substitution of a relatively large Fe\textsuperscript{2+} ion into a site could result in significant distortion.

Crystal slices were cut with the hexagonal c axis either in the plane of the slice (and therefore perpendicular to the \(\gamma\)-ray direction) or perpendicular to the slice and parallel to the \(\gamma\)-rays. Figure 2 shows spectra obtained at 4.2 K from such slices of the blue beryl referred to above. Ratios of the areas of the absorption peaks in the two configurations were obtained by fitting each spectrum with four unstrained lorentzian peaks, and values of these area ratios are given in table IIIa. These values are mean values obtained from measurements of four samples which had relatively low Fe\textsuperscript{3+}/Fe\textsuperscript{2+} concentration ratios (as indicated by optical absorption measurements): the small variability from sample to sample was ascribed to the effect of Fe\textsuperscript{3+} absorption near zero velocity.

Following Zory [10], the expected area ratios when each of the e. f. g. principal axes in turn is coincident with the c axis have been calculated as a function of the e. f. g. asymmetry parameter \(\eta\), taking into account the six-fold symmetry of the crystal about the c axis. The principal axes of the e. f. g. tensor \(\mathbf{V}\) are labelled in the conventional manner such that

\[ |V_{xx}| \geq |V_{yy}| \geq |V_{zz}| \]

and the asymmetry parameter \(\eta\), defined as

\[ (V_{xx} - V_{yy})/V_{zz} \]

is in the range \(0 \leq \eta \leq 1\). The results for \(\eta = 0, 0.5, 1.0\) are listed in table IIIb. It was assumed that \(V_{zz} < 0\) if it were positive all ratios would be inverted.

Comparison of the experimental results of table IIIa with the calculated ratios in table IIIb lead to the conclusion that the e. f. g. s at the two Fe\textsuperscript{2+} sites are consistent with the following:

- **Major site** \(V_{zz} < 0\) e. f. g. z axis parallel to c axis \(0 \leq \eta \leq 0.7\)
- **Minor site** \(V_{zz} < 0\) e. f. g. y axis parallel to c axis \(0.1 \leq \eta \leq 0.5\).
Thus, the Mössbauer spectra from the major site are consistent with $\text{Fe}^{2+}$ being substituted in the $\text{Al}^{3+}$ site. In such an octahedral site which has a trigonal compression along the c axis the $\text{Fe}^{2+}$ ion is expected to have an orbital singlet $^3\text{A}_1$ ground state and would give rise to an axially symmetric e. f. g. ($\eta = 0$) with a quadrupole splitting typically in the range $-2$ to $-4$ mm/s (the observed value was $-2.7$ mm/s) depending on the lattice e. f. g. contribution, the degree of covalency, the admixture of excited states into the ground state, etc. The spectra of figure 3 provide further evidence that $V_{zz}$ is negative for the $\text{Fe}^{2+}$ major site spectrum since they show that the low velocity peak of the doublet in zero field is associated with the $m_t = \pm \frac{1}{2}$ levels of the $^{57}\text{Fe}$ nuclear excited state.

We must be less definite about the assignment of the minor $\text{Fe}^{2+}$ site. By elimination it must be one of the tetrahedral sites if it is, in fact, substitutional. The isomer shift (Table I) is consistent with it being tetrahedral. We might favour the more strongly distorted $\text{Be}^{2+}$ site over the almost cubic $\text{Si}^{4+}$ site in view of the magnitude of the e. f. g. asymmetry parameter and also because the minor site e. f. g. has a relatively small temperature dependence: the quadrupole splitting decreased by only $\sim 0.1$ mm/s between 4.2 K and room temperature. This implies that the splitting of the cubic $^3\text{E}$ ground state is much greater than 300 K, which in turn indicates a site that is quite strongly distorted from tetrahedral symmetry. Finally, the fact that $\text{Fe}^{2+}$ appears to have a lower effective Debye temperature in the minor site than in the major site may suggest that it is replacing a much lighter ion in the minor site than in the major site. While this is again qualitatively consistent with the minor site being the $\text{Be}^{2+}$ site it should be pointed out that we have no real knowledge about relative force constants or their change on substituting an $\text{Fe}^{2+}$ ion into the sites.

It must be emphasized that the above discussion relies firstly on our supposition (based on the data of figure 4) that the two $\text{Fe}^{2+}$ sites are substitutional and secondly that substitution of $\text{Fe}^{2+}$ into the sites does not grossly affect their local point symmetry either directly by distortion or indirectly by attracting a local charge compensator.

3.4 Correlations between Mössbauer and optical data. — The strongest optical absorptions beyond the edge, viz. the $\sigma$-polarized band at 810 nm and the $\pi$-polarized composite band at 810 nm have been assigned to $\text{Fe}^{2+}$ ions in the octahedral $\text{Al}^{3+}$ site and in an interstitial channel site respectively [2]. The relative intensities of the $\pi$-polarized bands at 810 and 1 000 nm are always approximately the same from sample to sample and the two bands would therefore appear to arise from the same centre. The $\sigma$- and $\pi$-polarized bands at 810 nm, however, vary in relative intensity between samples and consequently originate from different centres. We have plotted the peak absorbances of the 810 nm $\sigma$- and $\pi$-polarized optical absorption bands in various samples against the normalized areas of the major and minor $\text{Fe}^{2+}$ site Mössbauer spectra to try to determine whether either or both of the optical bands can be attributed to single-ion transitions of $\text{Fe}^{2+}$ in the major or minor sites. These graphs are shown in figure 5. They indicate possible correlations between the major site area and the intensity of the $\pi$-band, and the minor site area and the intensity of the $\sigma$-polarized band. However, from the polarizations, energies and preliminary measurements of the temperature dependences of these optical absorption bands there are difficulties in assigning them to single-ion transitions of $\text{Fe}^{2+}$ in the $\text{Al}^{3+}$ and $\text{Be}^{2+}$ (or $\text{Si}^{4+}$) sites and it seems likely that the bands arise from more complicated processes such as charge transfer. Work is continuing in an attempt to clarify the origins of these optical absorption bands, although the above would indicate that the previous assignment [2, 3] of the $\sigma$-polarized band is incorrect.

3.5 Effects of heating. — Heating natural beryl samples at various temperatures produces a number of interesting effects that can be observed in optical and EPR spectra, and most appear to be associated with the annealing of various colour centres. These effects are not observed in the Mössbauer spectra and so will not be discussed further here. There is one heating effect that is observed by Mössbauer spectroscopy, however, and this occurs when samples are heated to $\sim 600$ °C, apparently regardless of the atmosphere in which they are heated [3]. This effect is characterized by the optical absorption, Mössbauer and EPR spectra shown in figure 6. These spectra are all from pieces of the same golden beryl.
FIG. 6. — The effect of heating a golden beryl crystal at 600 °C for 1 hour in air on its optical absorption, Mössbauer and EPR spectra. The spectra on the left are from single crystal pieces of a beryl sample before heat treatment and those on the right are from the same pieces after heating. The solid lines in the optical spectra (top) show absorption in \(\sigma\)-polarization and the dashed lines show the \(\pi\)-polarized spectrum. The sharp peaks in \(\pi\)-polarization are due to water. The sharp line in the EPR spectra (bottom) is from the \(m_s = -\frac{1}{2} \rightarrow +\frac{1}{2}\) transition of \(\text{Fe}^{3+}\).

crystal. Those on the left were recorded before any heat treatment, while those on the right are from the same crystal pieces after they had been heated at \(\sim 600 \, ^\circ\text{C}\) for 1 hour in air.

The optical absorption spectra show, firstly, the absorption edge at \(\sim 24,000 \, \text{cm}^{-1}\) moving to higher energy, causing the beryl to lose its golden colour: it turns blue because of the presence of the weak \(\pi\)-polarized band at 620 nm. This effect has been reported before [2, 3]. Secondly, the absorption bands attributed to \(\text{Fe}^{2+}\) — the \(\sigma\)-polarized band at 810 nm (12,350 cm\(^{-1}\)) and the \(\pi\)-polarized bands at 810 and 1,000 nm (12,350 and 10,000 cm\(^{-1}\)) — have increased in intensity, although the intensity of the \(\sigma\)-polarized band has increased more than that of the \(\pi\)-polarized doublet.

The Mössbauer results show that the areas of both the major and minor site \(\text{Fe}^{2+}\) spectra have increased on heating. Curve fitting indicates that this is a genuine increase in absorption in both sites rather than a redistribution of \(\text{Fe}^{2+}\) absorption intensity. While the absolute area increase in the major site spectrum is greater than that in the minor site spectrum, the latter appears to have increased by a larger proportion. This result supports the correlations suggested above between the optical and Mössbauer absorptions.

The EPR spectra show the sharp, strong absorption line corresponding to the \(m_s = -\frac{1}{2} \rightarrow +\frac{1}{2}\) transition of \(\text{Fe}^{3+}\) as well as weaker lines arising from other \(\text{Fe}^{3+}\) transitions, and indicate a decrease in the concentration of \(\text{Fe}^{3+}\) ions on heating. A similar result should also be obtainable using Mössbauer spectroscopy, as the \(\text{Fe}^{3+}\) absorption is clearly visible when magnetic fields are applied to a sample (Fig. 3). Such a measurement would allow a quantitative comparison of the changes in the \(\text{Fe}^{3+}\) and \(\text{Fe}^{2+}\) spectral areas, but unfortunately a magnet fault prevented this from being done in time to be included in this paper.

These measurements are the first real evidence of a heat-induced reduction of \(\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}\) in beryls. We cannot yet explain the mechanism involved, but much larger effects are observed in golden beryls than in others. This reduction process may not be responsible for the shift of the optical absorption edge, as has been previously postulated [2, 3] and this will be discussed in a future publication. Samoilovich et al. [3] failed to observe any effect of heat on their \(\text{Fe}^{3+}\) EPR signal, but their optical absorption bands were also unaffected. This has also occurred in some of the samples we have studied, but several have shown heating effects of varying magnitude similar to that illustrated in figure 6.

3.6 RELAXATION EFFECT. — A final point of interest concerns the temperature dependence of the \(\text{Fe}^{3+}\) major site Mössbauer spectrum. The spectra of a powder sample of an aquamarine beryl at 4.2 K, 77 K, and 295 K are shown in figure 7. At 4.2 K both of the major site absorption peaks are very narrow (\(\sim 0.21 \, \text{mm/s}\)), but at 77 K the low-velocity line has broadened to a greater extent than has that

FIG. 7. — Mössbauer spectra of a powder sample of an aquamarine beryl at 4.2 K, 77 K and 295 K. The source was \(^{57}\text{CoFe}\) at room temperature.
at higher velocity. There is little change on further heating to 295 K. The two peaks of the minor site spectrum remain of equal width throughout this temperature range, as has been verified with a sample with a much more intense minor site spectrum than that in figure 7. This broadening effect has been observed in all samples studied so far, and it appears to be due to a relaxation effect, but experiments aimed at establishing its origin have not yet been completed. A similar relaxation effect for Fe$^{2+}$, although in a site of rather different symmetry, has been reported in the mineral gillespite [7].

4. Conclusions. — Two independent Fe$^{2+}$ sites and one Fe$^{3+}$ site have been observed in natural beryl crystals using Mössbauer spectroscopy. The Fe$^{2+}$ ions appear to occupy two substitutional sites in the lattice, one of which is octahedral (Al$^{3+}$) and the other tetrahedral (Be$^{2+}$ or Si$^{4+}$).

Evidence for a heat-induced reduction of Fe$^{3+} \rightarrow$ Fe$^{2+}$ in both of these substitutional sites was obtained and this would appear to indicate that Fe$^{3+}$ also occupies both substitutional sites. However, evidence of conservation of total substitutional iron (i.e. Fe$^{3+} +$ Fe$^{2+}$) Mössbauer absorption has not yet been obtained.

In contrast to previous assignments, the intensities of optical and Mössbauer absorption peaks in various samples indicated a possible association of the 810 nm $\sigma$-polarized optical band with Fe$^{2+}$ in the minor (tetrahedral) site, and of the $\pi$-polarized bands at 810 nm and 1 000 nm with Fe$^{2+}$ in the major (octahedral) site, although group theoretical considerations make assignment of the optical bands to single-ion Fe$^{2+}$ transitions difficult.

We saw no evidence of Fe$^{2+}$ ions in the structural channels; such ions have been postulated by Wood and Nassau [2] to explain the $\pi$-polarized band at 810 nm. However, if they were present, these Fe$^{2+}$ ions would be expected to have a small recoilless fraction and as a result might not be observable in the Mössbauer spectra.

References