The Mössbauer Spectrum of Almandine

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Abstract. Mössbauer spectra of a synthetic, pure almandine (Alm_{100}) and a natural almandine-rich garnet (Alm_{86}) were taken at temperatures between 295 and 4.2 K.

Different widths and depths of the lines observed in the paramagnetic state require the spectra to be fitted with at least two components of slightly different quadrupole splittings and isomer shifts.

Alm_{100} shows a gradual onset of magnetic order between 10.4 and 9.0 K, with about 50 percent of the sample magnetically ordered at 9.6 K. At 4.2 K both samples have complex spectra that can be fitted by two eight-line magnetic hyperfine patterns of equal intensities. These result from the existence of two different polar angles between the z-axis of the electric field gradient and the direction of the magnetic hyperfine field, or from two distinctly different electric field gradients. The former interpretation, in which the two angles are attributed to a modulated, non-collinear spin arrangement, is considered more likely.

Both magnetic components have practically identical quadrupole splittings, $\frac{1}{2}eQV_{zz}(1+\eta^2/3)^{\frac{1}{2}}$, that average -3.70 mm·s^{-1}, and a small asymmetry parameter of $\eta = 0.07$. Alm_{100} has a magnetic hyperfine field of 25.7 T at 4.2 K, whereas Alm_{86} has a hyperfine field of only 23.3 T; the other features of the spectra of both samples are similar.

Introduction

Pure almandine, $Fe_3Al_2(SiO_4)_3$, contains 43.30 weight percent FeO, corresponding to 33.66 weight percent Fe^{2+}. Fe is located exclusively in the eightfold-coordinated $24c$ position of the space group $Ia3d$. Natural almandines tend to contain significant proportions of other garnet end members, in particular pyrope, spessartine and grossular. As a result of this, physical data determined on natural "almandines" may be strongly influenced by contributions from other constitutent garnet end members, and thus not represent values for almandine *sensu stricto*.

The ^{57}Fe Mössbauer spectra of paramagnetic silicate garnets that contain Fe^{2+} in the $24c$ position have been reviewed by Amthauer et al. (1976). Typical Mössbauer parameters for almandine at room temperature are a large quadrupole splitting ΔE_Q of about -3.5 mm·s^{-1} and an isomer shift δ/Fe of about $+1.3$ mm·s^{-1} relative to metallic iron. Mössbauer spectra of natural paramagnetic garnets of different compositions show hardly any variation of the isomer shift and quadrupole splitting of Fe^{2+} in the $24c$ position as Fe is replaced by other elements, *e.g.* Mg or Mn,

even if these substitutions amount to over 50 percent. Minor amounts of Fe^{2+} in the $24c$ position of pyrope or spessartine, for example, also give parameters similar to those of pure almandine. Mössbauer spectra taken in the paramagnetic state therefore have little diagnostic capacity for characterization of the occupancy of the $24c$ position in Fe^{2+}-bearing garnets.

Even a minor replacement of Fe^{2+} by ions with different magnetic properties (*e.g.* Mg^{2+}, Ca^{2+} or Mn^{2+}) should, however, cause noticeable changes in the magnetic behaviour, like the Néel temperature and the magnetic hyperfine field. The magnetic properties of garnets are therefore expected to be much more sensitive to such compositional variations than the quadrupole interaction. Such changes can be observed by Mössbauer spectroscopy at sufficiently low temperatures.

An essential requirement for the interpretation of Mössbauer spectra of magnetically ordered garnets is knowledge of the parameters for the end-members. The present study was carried out to determine parameters characterizing the magnetic properties of pure almandine, and thus to ascertain whether Mössbauer spectra taken in the magnetically ordered state of garnets containing Fe^{2+} in the $24c$ position give more information on the substitution of Fe than spectra of paramagnetic material.

Prandl (1971) found a natural "almandine" of composition $Alm_{79}Py_{18}Sp_2Gro_2$ to have a Néel temperature of about 7.5 K. The same sample had a magnetic hyperfine field of 22.8 ± 0.4 T at 4.2 K (Prandl and Wagner 1971). In the present paper we describe Mössbauer spectra of a synthetic, essentially pure almandine at room temperature, in the neighbourhood of the Néel temperature (between 11.0 and 9.0 K), and at 4.2 K. Supporting measurements were carried out on a natural almandine-rich garnet in which 14 percent of the $24c$ sites are occupied by diamagnetic ions.

Experimental

One of the two samples studied (Alm_{100}) was prepared by reacting a glass of almandine composition, with the oxygen fugacity controlled by an iron-wüstite buffer, at 900° C and 15 kbar (Bohlen et al. 1983). Except for a minor Fe^{3+} content (see below), this sample is essentially pure almandine. The second sample, USNM # 107105-2, was a natural almandine-rich garnet from Idaho. Novak and Gibbs (1971), who carried out a detailed crystallographic study

Table 1. Mössbauer parameters of the studied almandines at selected temperatures

Sample	T(K)	ΔE_Q	δ/Fe	W	η	θ	B_{hf}
Alm_{100}	295	−3.513 (1)	1.286 (1)	0.277 (1)			−
	295[a]	−3.536 (6)	1.267 (4)	0.268 (1)			−
		−3.491 (6)	1.304 (4)	[b]			−
	78	−3.668 (1)	1.421 (1)[c]	0.264 (1)			−
	11.0	−3.647 (1)	1.423 (1)[c]	0.267 (1)			−
	4.2	−3.692 (9)	1.324 (2)	0.350 (2)[d]	0.03 (1)	90 (2)	26.13 (3)
		−3.701 (6)	1.294 (2)	0.332 (3)[d]	0.12 (1)	73.1 (1)	25.20 (2)
	4.2[e]	−3.356 (6)	1.386 (2)	0.353 (3)[d]	0.10 (1)	79.0 (1)	25.28 (2)
		−4.022 (7)	1.232 (2)	0.339 (3)[d]	0.04 (1)	80.8 (1)	26.02 (2)
Alm_{86}	294	−3.527 (1)	1.283 (1)	0.277 (1)			−
	294[a]	−3.543 (2)	1.253 (4)	0.259 (1)			−
		−3.508 (2)	1.315 (2)	[b]			−
	78	−3.659 (1)	1.418 (1)[c]	0.270 (1)			−
	4.2	−3.699 (9)	1.351 (3)	0.428 (7)[d]	0.00 (1)	84.6 (2)	23.66 (3)
		−3.61 (2)	1.274 (3)	0.445 (7)[d]	0.16 (1)	76.5 (2)	23.00 (6)
	4.2[e]	−3.41 (2)	1.349 (3)	0.481 (7)[d]	0.13 (1)	81.5 (2)	22.75 (7)
		−3.843 (9)	1.293 (2)	0.404 (5)[d]	0.03 (1)	80.8 (1)	23.76 (3)

Parameters for $24c$ almandine component only; for Fe^{3+} components see text

Quadrupole splittings $(\Delta E_Q = \frac{1}{2}eQ V_{zz}(1+\eta^2/3)^{\frac{1}{2}})$, isomer shifts (δ/Fe) and line widths (W) given in $mm \cdot s^{-1}$, polar angles (θ) in degrees, magnetic hyperfine fields (B_{hf}) in T. Errors on last digit given in parentheses

[a] Alternative fit using two doublets
[b] Line widths of both constituent spectra constrained to be equal
[c] Only absorber cooled; source at room temperature
[d] Line widths constrained to be equal within each subspectrum
[e] Alternative fit to spectrum of magnetically ordered sample

of the same garnet, gave its composition as $Alm_{86}Py_9Gro_4$; this sample is designated Alm_{86} here.

For Mössbauer spectroscopy both samples were finely ground in an agate mortar. Absorbers were prepared by placing 30 mg of the powder in a Lucite holder of 2 cm² area, giving Fe densities of about 5 mg·cm⁻². To check for saturation effects an additional spectrum of Alm_{100} was taken using a thinner absorber containing only 13 mg of the sample at 4.2 K. Mössbauer spectra were taken at room temperature, between 78 and 9.0 K using a cryostat in which only the absorber was cooled, and at 4.2 K using a bath cryostat in which both source and absorber were immersed in liquid helium. The ⁵⁷Co/Rh Mössbauer source was moved in a sinusoidal mode. The radiation transmitted by the absorber was detected by a Kr proportional counter and stored in a 1,024-channel analyzer. A 6 μm thick metallic Fe foil was used for velocity calibration; all isomer shifts are referred to the centroid of the room-temperature spectrum of this foil.

Superpositions of Lorentzian lines were fitted to the spectra using a CDC Cyber 875 computer. The spectra of the magnetically ordered garnets were fitted with a program that calculated the positions and intensities by diagonalizing the full hyperfine Hamiltonian.

Results

At 295 and 78 K the Mössbauer spectra of Alm_{100} and Alm_{86} consist essentially of asymmetric doublets, the high-velocity peaks of which (corresponding to the $m_I \pm \frac{1}{2} \rightarrow$
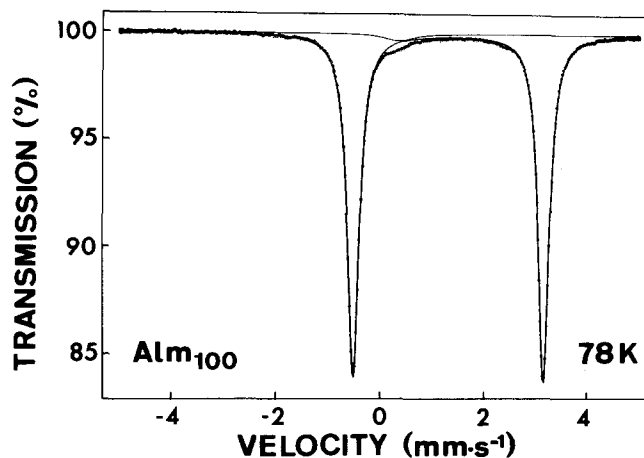

Fig. 1. Mössbauer spectrum of pure synthetic almandine (Alm_{100}) at 78 K fitted with two independent Lorentzians for the almandine component (plus an additional single-line component)

$\pm\frac{1}{2}$ transition) are narrower and have a lower transmission than the low-velocity peaks. Due to the second-order Doppler effect the shifts, δ/Fe, are higher at 78 K than at room temperature; the values of ΔE_Q have also increased somewhat (Table 1).

Both spectra also show weak, additional components, that may be either unresolved paramagnetic doublets or the high-velocity lines of such doublets. In Alm_{100} a broad peak was observed, with δ/Fe = 0.43(1), W = 0.68(5) mm·s⁻¹ and a relative area of 2.7(2) percent at 78 K (Fig. 1). Doub-
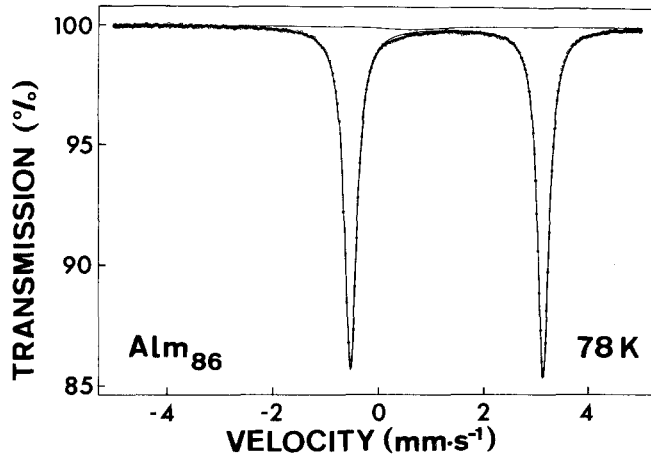
Fig. 2. Mössbauer spectrum of natural almandine-rich garnet (Alm_{86}) at 78 K fitted with two independent Lorentzians for the almandine component (plus an additional single-line component)
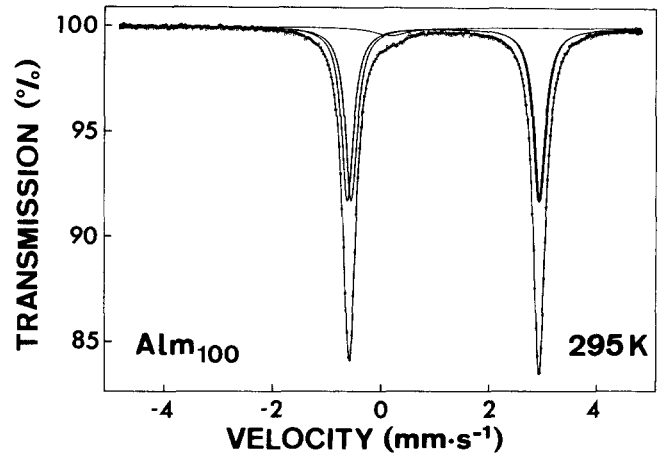

Fig. 3. Room-temperature Mössbauer spectrum of Alm_{100} fitted with two doublets constrained to have equal widths and, within each doublet, equal intensities (plus an additional single-line component)

Table 2. Line widths of paramagnetic garnets at different temperatures

Sample	$T(K)$	W_l	W_h	W_l/W_h
Alm_{100}	295	0.2835 (9)	0.2682 (7)	1.057 (4)
	78	0.2715 (6)	0.2559 (4)	1.061 (3)
	11	0.2699 (8)	0.2647 (7)	1.020 (4)
Alm_{86}	293	0.2878 (8)	0.2663 (7)	1.081 (4)
	78	0.2791 (7)	0.2619 (5)	1.066 (3)

Widths from single-Lorentzian fits to each line; parameters are given only for the $24c$ Fe^{2+} components

W_l, W_h: widths of low-velocity and high-velocity lines in $mm \cdot s^{-1}$

Errors on last digit given in parentheses

let fits to this component were also possible. Because the low-velocity peak of this doublet and that of almandine partly overlapped, the parameters of these fits (e.g., $\delta/Fe = 0.20$, $\Delta E_Q = 0.69$, $W = 0.48$ $mm \cdot s^{-1}$ at 77 K) are, however, somewhat tentative. In Alm_{86} an additional broad peak with $\delta/Fe = 0.70(6)$ $mm \cdot s^{-1}$, $W = 1.3(2)$ $mm \cdot s^{-1}$ and a relative area of 2.1(3) percent at 78 K (Fig. 2) could not be resolved into a doublet. These weak and poorly developed components probably result from Fe^{3+} in the garnet structure. Since they have no direct association with the almandine spectra s.s., these components will not be discussed here any further.

The asymmetries of the almandine doublets are strongly developed at room-temperature and at 78 K, but were considerably reduced in Alm_{100} at 11.0 K (Table 2). Rather poor fits ensue if the asymmetric spectra are fitted with doublets constrained to have equal widths and intensities. These are therefore usually fitted with two Lorentzians of different widths and depths. Such an unconstrained fit of the room-temperature spectrum of Alm_{100} gave widths of 0.284(1) and 0.268(1) $mm \cdot s^{-1}$ for the low- and high-velocity peaks, respectively. The areas of these peaks, however, differed by only 1.7 percent because the depths vary inversely. Such unconstrained fits give improved agreement with the experimental data compared to fits of doublets con-

strained to have equal widths and intensities (reducing χ^2 from 1.54 to 1.07 for Alm_{100}, and from 2.21 to 1.35 for Alm_{86} at room temperature), but they suffer from the inherent weakness that they offer no explanation for the spectral asymmetry.

Fitting the room-temperature spectra with two doublets, each of which was constrained to have lines of equal widths and dips (plus an additional line for the Fe^{3+} component) resulted in significant improvements compared to fits with only one "constrained" doublet, reducing χ^2 at room temperature for Alm_{100} from 1.54 for a one-doublet fit to 1.04, and for Alm_{86} from 2.21 to 1.11. The two doublets of these fits have similar intensities, but slightly different quadrupole splittings and isomer shifts (Table 1). Figure 3 shows the high-velocity peaks of these doublets to be closer together than the low-velocity peaks, thus producing asymmetric spectra. Reduced differences in isomer shifts cause the observed decrease in asymmetry as temperatures are lowered.

At 4.2 K Alm_{100} is magnetically ordered with relatively narrow lines. This facilitates analysis of the spectrum (Fig. 4), which is more complex than that reported for a natural garnet containing 79 percent of the almandine component by Prandl and Wagner (1971), who interpreted their data in terms of a single Fe site. The spectrum observed here can be fitted by two slightly different eight-line patterns of equal intensities. This means that although Fe^{2+} ions occupy only one $24c$ position in almandine, two non-equivalent Mössbauer sites exist in the magnetically ordered state. A comparison of spectra taken on absorbers with iron densities of 5.0 and 2.2 $mg \cdot cm^{-2}$ showed no noticeable saturation effects.

Two practically equally good fits of the spectra (χ^2 5.79 and 6.31 for models 1 and 2, respectively) can be obtained with slight differences of the subspectra (Table 1), that are attributed to either

– 1) the existence of two different polar angles θ of 73 and about 90° between the directions of B_{hf} and the principal ($z-$) axis of the electric field gradient tensor, while both components have nearly identical quadrupole splittings $\frac{1}{2}eQ V_{zz}(1 + \eta^2/3)^{\frac{1}{2}}$ of -3.70 $mm \cdot s^{-1}$; or
– 2) the existence of two distinct quadrupole splittings

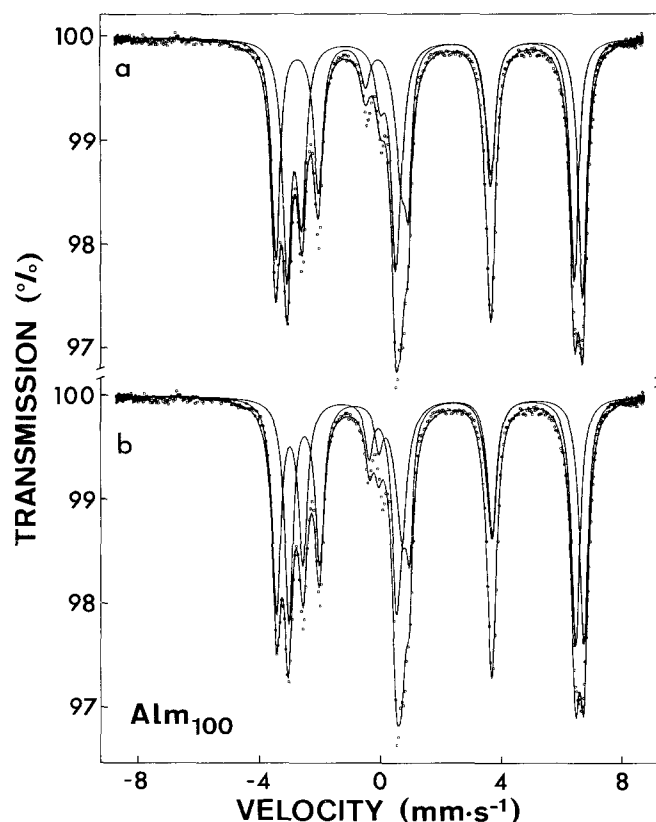**Fig. 4a, b.** Mössbauer spectrum of Alm_{100} at 4.2 K fitted with two hyperfine patterns that differ mainly (**a**) in the angles θ between the z-axis of the electric field gradient and the magnetic hyperfine field, and (**b**) in their quadrupole splittings

of -3.36 and -4.02 mm·s^{-1}, but nearly identical polar angles θ of $80°$.

In both cases the asymmetry parameter η is quite low, showing the electric field gradient at the $24c$ sites to be almost axially symmetric. Because of the low value of η, the azimuthal angle ϕ between V_{xx} and the projection of B_{hf} on the x-y plane is of little significance; ϕ was therefore held fixed at zero during the fitting procedure. Other parameters of this spectrum are similar hyperfine fields B_{hf} averaging 25.7 T and a mean line width of 0.34 mm·s^{-1}.

Alm_{100} has rather complicated Mössbauer spectra in the vicinity of the Néel temperature. While it is completely paramagnetic down to 11.0 K, wings have developed on the sides of the Fe^{2+} lines at 10.4 K, indicating incipient magnetic order. The contribution of a magnetically ordered component to the Mössbauer spectra of this sample becomes more pronounced as the temperature decreases below 10.0 K (Fig. 5). At 9.6 K, 50 percent of the total spectral area can be assigned to a magnetically ordered phase (Fig. 6). At 9.0 K no indication of a paramagnetic phase remains, but the spectrum has lines of different – partly rather high – widths, suggesting the existence of hyperfine field distributions. The mean magnetic hyperfine field at 9.0 K is about 12.5 T.

On the basis of a Néel temperature of 10 K and the hyperfine field at 4.2 K, the saturation hyperfine field of Alm_{100} was calculated by extrapolation of a Brillouin function for high-spin Fe^{2+} ($3d^6$, $S=2$) as 26.9 T.

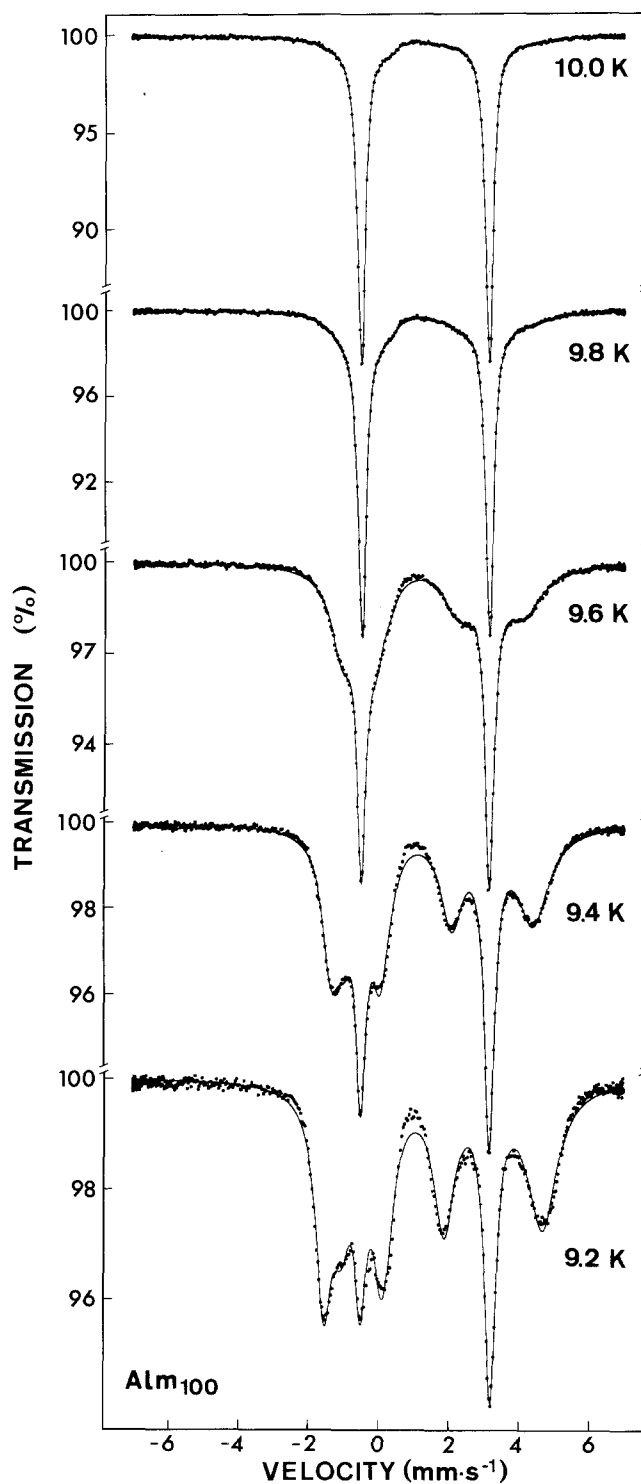The Mössbauer spectrum of Alm_{86} at 4.2 K (Fig. 7)

Fig. 5. Mössbauer spectra of Alm_{100} in the neighbourhood of the Néel temperature, showing the gradual onset of magnetic order. To obtain an indication of the degree of magnetic order, the spectra were fitted with up to 8 independent Lorentzians

resembles that of Alm_{100}. Major differences are a lower magnetic hyperfine field of about 23.3 T and higher line widths averaging 0.44 mm·s^{-1}. Because of the wider lines, differences between the two constituent subspectra are less pronounced than in Alm_{100}. The wide lines furthermore result in poorer fits and higher errors for the individual parameters of Alm_{86} (cf. Table 1) than for those of Alm_{100}.
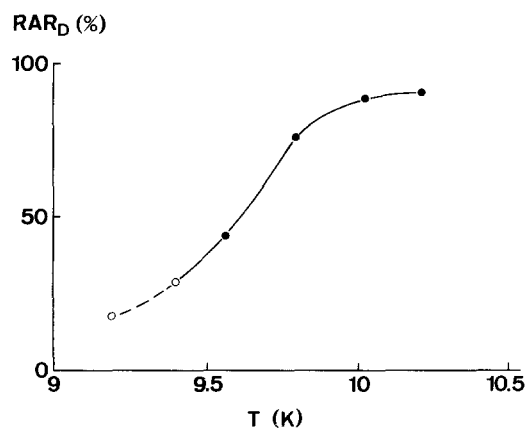
RAR$_D$ (%)

Fig. 6. Relative contribution of doublet (RAR$_D$) to the total spectral area of Alm$_{100}$ in the neighbourhood of the Néel temperature on the basis of spectra shown in Figure 5
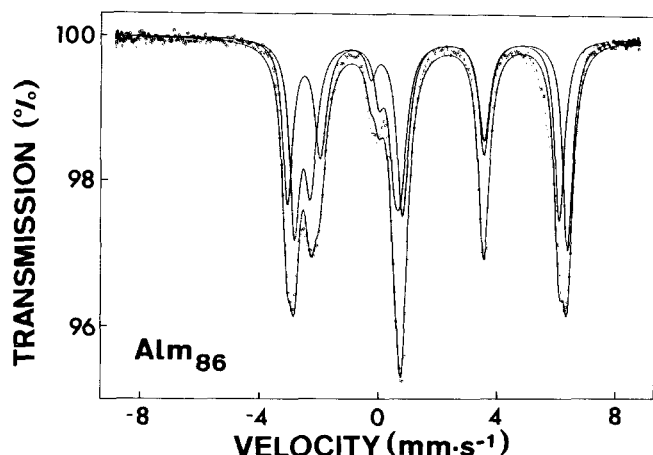

Fig. 7. Mössbauer spectrum of Alm$_{86}$ at 4.2 K fitted with two hyperfine patterns that differ mainly in the angles θ between the z-axis of the electric field gradient and the magnetic hyperfine field

Discussion

The asymmetric spectra observed at room-temperature could be satisfactorily fitted using a two-doublet model with slightly different isomer shifts and quadrupole splittings. The two-doublet fits *need* not reduce χ^2 significantly beneath the values of the "unconstrained" two-line fits to be preferable, since they provide a physically rational explanation for the spectral asymmetry. Such an approach has also been successfully applied to the analysis of complex Mössbauer spectra of paramagnetic titaniferous garnets showing charge transfer phenomena (Schwartz et al. 1980).

Amthauer et al. (1976) described a similar asymmetry for Fe^{2+} in the *24c* position of paramagnetic garnets, and attributed this to paramagnetic relaxation. The high Fe content of the garnets studied here, as well as the observation that the asymmetry is reduced at low temperatures, render such an interpretation improbable in the present case. Kan et al. (1986) observed no dependence of this asymmetry on garnet composition within the pyrope-almandine series, indicating that this is not a result of next-nearest neighbour effects. The similar areas of the two resonant lines also

show that the line asymmetry cannot result from a Goldanskii-Karyagin effect.

A possible cause for the peak asymmetry may be the existence of slightly different Fe^{2+} sites in the garnet structure. Although the existence of different sites seems to be contradictory to the cubic crystal symmetry, careful X-ray diffraction work by Chenavas et al. (1978) has shown that deviations from cubic symmetry are quite common in garnets. Dempsey (1980) and Takéuchi et al. (1982) have shown that lattice distortions may cause the atomic sites of space group *Ia3d* to degenerate into inequivalent and slightly displaced sites. The two doublets to which the paramagnetic spectra were fitted moreover need not necessarily correspond to *two* distinct Fe sites in the almandine structure. It is conceivable that the two-doublet fits are merely simplified approximations for more than two different Fe sites, or possibly even distributions of Fe sites with a negative correlation between the isomer shifts and quadrupole splittings. Such site distributions could be caused by sample inhomogeneities on an atomic scale, leading to a variety of slightly different next-nearest neighbour configurations.

The Néel temperature of Alm$_{100}$ is smeared out over the temperature range between 10.4 and 9.0 K. The mean Néel temperature is taken as that temperature at which 50 percent of the spectral area of Alm$_{100}$ can be assigned to a magnetically ordered phase, *i.e.* 9.6 K. The temperature range over which Alm$_{100}$ orders magnetically (*ca.* 1.4 K) is considerably wider than that observed for andradite (*ca.* 0.5 K; Murad 1984), and may be due to an inhomogeneous distribution of impurities – possibly the Fe^{3+} contained in this sample. No spectra of Alm$_{86}$ were taken in this temperature range. It can, however, be considered certain that the Néel temperature of Alm$_{86}$ is lower than 9.6 K, since Fe – O – Fe superexchange will be reduced when Fe^{2+} is replaced by diamagnetic ions (Mg^{2+} and Ca^{2+} in this case).

The two alternative fits of the Mössbauer spectra of Alm$_{100}$ in the magnetically ordered state attribute the existence of two magnetic patterns to different causes, namely:

– 1) The existence of two different angles, θ, between the hyperfine field and V_{zz}. This indicates a non-collinear spin arrangement, in which the Fe spins are oriented at angles of 73° and 90° to the z-axis of the electric field gradient, which is directed along the crystallographic [110] directions.

– 2) The existence of two significantly different quadrupole splittings ΔE_Q of -3.36 and -4.02 mm·s^{-1}. This would indicate two crystallographically non-equivalent sites to exist in the magnetically ordered state.

It is not readily understandable how magnetic order could bring about the two distinctly different electric field gradients required by the second solution, whereas the field gradients above the Néel temperature show only minor variations. The first interpretation is therefore considered more likely.

Prandl and Wagner (1971) took Mössbauer spectra of a natural almandine-rich garnet at different temperatures. At 4.2 K this was magnetically ordered; the spectrum was fitted with one set of eight, very wide ($W=0.88$ mm·s^{-1}) lines. Other parameters of this fit were a quadrupole splitting of $-3.46(9)$ mm·s^{-1} and a magnetic hyperfine field of 22.8(4) T, a value that is slightly lower than that found here for Alm$_{86}$. Prandl and Wagner (1971) interpreted their

data as indicating one Fe site with the magnetic hyperfine field directed perpendicular to the z-axis of the electric field gradient tensor.

The 4.2 K-spectrum of Alm_{86} taken here appears to be intermediate between that of Alm_{100}, with two distinct, well-defined components, and that of the garnet described by Prandl and Wagner (1971), whose lines were very broad, not allowing distinction of two components. Several causes may add up to produce the significantly wider lines and lower hyperfine fields in the substituted almandines compared to Alm_{100} at 4.2 K:

— The lowering of Néel temperatures caused by substitution results in higher reduced temperatures, T/T_N, at 4.2 K. The distribution of Néel temperatures which was observed even in Alm_{100} (and probably becomes wider with increasing substitution) thus causes a wider distribution of hyperfine fields in the 4.2 K-spectra of substituted garnets.

— Substitution may affect the magnitude and direction of the hyperfine field directly. The effect on the direction of the field will lead mainly to a smearing out of the structure of the group of four lines around $-2.5\ mm \cdot s^{-1}$ (Fig. 7).

Conclusions

Pure almandine appears to have a canted spin structure, which is more complicated than that observed by Prandl (1971) for a substituted almandine-rich garnet. In this spin structure two different angles exist between the z-axis of the electric field gradient and the hyperfine field. These angles, and possibly also other parameters, become smeared out on substitution of the garnets.

The existence of the two magnetic sites below the Néel temperature is not necessarily related to the asymmetric quadrupole patterns observed above the Néel temperature. It is, however, conceivable that deviations from cubic symmetry are responsible for either or both of these effects.

The observed variations of the Mössbauer parameters of almandine at 4.2 K as Fe on the $24c$ site is replaced by other atoms bears out the conception that Mössbauer spectra taken in the magnetically ordered state should react more sensitively to such substitutions than spectra taken on paramagnetic garnets. Mössbauer spectra of magnetically ordered garnets thus have more diagnostic capacity for such substitutions.

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