Atomic Displacement Parameters for Garnets: A Lattice-Dynamical Evaluation

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Abstract

Atomic displacement parameters (a.d.p.'s), together with vibrational spectra (Raman and IR) and thermodynamic functions, have been calculated for some minerals of the garnet group, such as pyrope ($Mg_3Al_2Si_3O_{12}$), grossular ($Ca_3Al_2Si_3O_{12}$), andradite ($Ca_3Fe_2Si_3O_{12}$) and almandine ($Fe_3Al_2Si_3O_{12}$). For this purpose, a rigid-ion Born–von Karman model has been applied, using empirical atomic charges and valence force fields derived from a best fit to the vibrational spectra of a group of orthosilicates and oxides. Agreement with the experimental data is good, with the only exception of pyrope and almandine: for these minerals the calculated a.d.p.'s of the Mg^{2+} atom in the former and of the corresponding Fe^{2+} atom in the latter are too low. This result confirms the unusual behaviour of these atoms, for which dynamic disorder has been claimed. However, if the values of the specific heat and entropy are considered and compared with our calculations, this situation can be best explained assuming the transition to static disorder of the Mg^{2+} and Fe^{2+} atoms to occur at low temperature.

1. Introduction

Besides providing the possibility of verifying the physical meaning of the corresponding data obtained from crystal structure refinement, the calculation of atomic displacement parameters (a.d.p.'s or U's) for minerals and similar inorganic solids can be particularly useful for checking the general validity of the model and of the force fields employed to interpret the vibrational behaviour of these substances.

In view of the essential success we achieved for some oxides and also orthosilicates of the olivine group [Pilati, Bianchi & Gramaccioli, 1990b: here onwards PBG90; Pilati, Demartin & Gramaccioli, 1993 (PDG93); Pilati, Demartin, Cariati, Bruni & Gramaccioli, 1993 (PD-CBG); Pilati, Demartin & Gramaccioli, 1994 (PDG94); Pilati, Demartin & Gramaccioli, 1995a (PDG95a)], we thought to extend our calculations to another particularly important group of orthosilicates, *i.e.* garnets. Our project was suggested by the need for a wider check of these lattice-dynamical procedures, as applied to a

considerable number of other substances; a major point was also that of examining the possibility of transferring these force fields (or empirical force fields in general) within silicates. In addition, as we will see, there are certain physico-chemical problems which are typical of some garnets, involving non-trivial applications of crystallography.

Since garnets are very interesting to both mineralogy and petrology, and also to materials science and physical chemistry in general, accurate experimental data of various types are relatively abundant. Referring to the pure silicate end-members only, there are a number of accurate crystal structure determinations, sometimes at different temperatures [see, for instance, Armbruster, Geiger & Lager, 1992: hereinafter AGL; Geiger, Armbruster, Lager, Jiang, Lottermoser & Amthauer, 1992 (GALJLA); Sawada, 1993; Ungaretti, 1994]; in addition, several experimental measurements of many physical properties have also been reported in the literature. These data include Raman, IR and NMR spectra (see, for instance, Hofmeister & Chopelas, 1991a: hereinafter HFC; McMillan, Akaogi, Ohtani, Williams, Nieman & Sato, 1989; Geiger, Winkler & Langer, 1989; Geiger, Merwin & Sebald, 1992: from here onward GMS; Gillet, Fiquet, Malézieux & Geiger, 1992), Mössbauer spectra (see, for instance, Amthauer, Annersten & Hafner, 1976; Murad & Wagner, 1987; GALJLA), as well as values of thermodynamic functions (see, for instance: Metz, Anovitz, Essene, Bohlen, Westrum & Wall, 1983; Madon, Gil Ibarguchi, Via &·Girardeau, 1991; Westrum, Essene & Perkins, 1979; Haselton & Westrum, 1980; Robie, Bin, Hemingway & Barton, 1987; Tequi, Robie, Hemingway, Neuville & Richet, 1991; Anovitz, Essene, Metz, Bohlen, Westrum & Hemingway, 1993).

As for all crystalline substances, lattice-dynamical calculations for garnets can provide a general interpretation of the vibrational spectra using a consistent overall model: in this way, the selection of the fundamentals from the experimental Raman or IR data can be confirmed. Furthermore, the possibility of deriving the values of thermodynamic functions by applying statistical mechanics, using the phonon density of states obtained from a calculation extended to the whole Brillouin zone,

is particularly interesting: this procedure is essentially similar (and parallel) to the calculation of atomic thermal parameters and can be carried out at the same time, as a by-product of the same routine (see, for instance, PDG93). These estimates of thermodynamic functions can be compared with those obtained by other authors using similar methods, such as the lattice-dynamical calculations in connection with energy-minimization carried out by Winkler, Dove & Leslie (1991), Patel, Price & Mendelssohn (1991) or, again, with the results of much simpler statistical mechanical procedures.

Of such procedures, Kieffer's method (Kieffer, 1979, 1980) can be considered as an extension of Debye's model, including a contribution from optic modes, whose frequencies are assumed to be constant throughout the Brillouin zone and are essentially derived from agreement with Raman or IR measurements; owing to its simplicity, it is often employed for deriving values of thermodynamic functions from spectroscopic data, especially by geologists and mineralogists: there are examples of its application to garnets, such as pyrope and grossular (Hofmeister & Chopelas, 1991b) and also andradite (Madon et al., 1991). However, apart from the exceedingly approximate basic assumptions of the method, a definite drawback for its application to garnets in particular is that for these substances more than half the frequencies at the origin of the Brillouin zone are both IR- and Raman-inactive; therefore, too many further assumptions are necessary. Such a considerable total number of assumptions renders the whole matter not fully reliable from a physical point of view, in spite of it being accepted and used by several scientists. Examples of this situation are given below.

Of the whole garnet group, only those pure end members for which reliable experimental estimates of the U's are available in the literature have been considered in the present work. In one case (andradite, $Ca_3Fe_2Si_3O_{12}$) the crystal structure has been refined using new data from a pure natural sample.

For some garnets there are particular problems: for instance, pyrope ($Mg_3Al_2Si_3O_{12}$) appears to have an anomalously high heat capacity at low temperatures (see, for instance, Kieffer, 1980; Haselton & Westrum, 1980; Hofmeister & Chopelas, 1991b). In their lattice-dynamical calculations Winkler et al. (1991) confirm this anomalous behaviour, since their estimation of entropy at room temperature (237.3 J mol^{-1} K) is too low (see Table 6): according to these authors, such a discrepancy is due to the essential anharmonic motion of the Mg atom, whose eightfold 'distorted cubic' coordination is quite unusual; a similar conclusion based on spectroscopic grounds was reached by GMS. This unusual behaviour of the Mg atom has also been confirmed by X-ray diffraction studies, especially by AGL and Sawada (1993): the latter author had to apply the Gram–Charlier series expansion up to the fourth-rank tensor to account for the atomic displacement

satisfactorily. In their lattice-dynamical work, Patel et al. (1991) also find a notable disagreement in the low-temperature simulations for pyrope, in contrast to generally very good agreement for other silicates. This disagreement is ascribed to the effect of a particularly limited sampling of the Brillouin zone, where only eight points were considered for saving computing time in view of the large unit cell. However, as we will see, such disagreement is evident even in our calculation where a thicker sampling (64 points) has been used.

Similar problems are encountered for almandine ($Fe_3Al_2Si_3O_{12}$). Here, modelling of the lattice contribution to entropy performed by Metz et al. (1983) and Anovitz et al. (1993) has revealed the presence of significant excess entropy above that attributable to the magnetic transition ($3R\ln 5$): according to these authors, this excess entropy might be ascribed to a low-temperature electronic transition or Schottky contribution. A distinct asymmetry of the Fe^{2+} quadrupole split doublet in the Mössbauer spectrum has also been noticed in several papers: this asymmetry has been ascribed to various reasons, such as magnetic relaxation (Amthauer et al., 1976), or (by GALJLA) the Gol'danskii–Karyagin effect (Gol'danskii, 1964): for a review of the matter, see GALJLA. However, in an independent study of the problem, Murad & Wagner (1987) exclude the Gol'danskii–Karyagin effect, because the two resonant lines in the Mössbauer spectrum have similar areas: these authors would rather imply the observed asymmetry to be due to possible deviations from cubic symmetry. This observation is important with respect to our conclusions (see below). As with the Mg atom in pyrope, the unusual behaviour of the Fe atom in almandine is also evident on examining thermal parameters obtained from accurate X-ray crystal structure determinations (AGL; GALJLA). The above listed phenomena for pyrope and almandine are quite likely to be connected to each other, in view of the ionic radius for Mg^{2+} or Fe^{2+}, which is too small with respect to that of the corresponding atoms in other garnets.

These observations have considerably increased our interest in performing lattice-dynamical calculations for garnets using our own techniques and potentials. In particular, the unusual vibrational behaviour of some atoms should be evident by comparison of the crystal-structure estimates of the U's with those obtained from our calculations, which assume harmonic motion. Further useful information can be provided by considering the estimates of entropy and other thermodynamic functions as a function of temperature.

2. Experimental measurements

Experimental details are summarized in Table 1. For our purposes, a crystal of andradite (demantoide) from Val Malenco measuring ca $0.15 \times 0.15 \times 0.10$ mm was used. Chemical analysis at the microprobe (Corbelli,

1993) showed it to be essentially pure, with trace amounts of Cr_2O_3, TiO_2, MnO and Al_2O_3 (0.01–0.1%), and MgO (ca 0.4%).

A total of 2174 diffracted intensities were collected at room temperature (293 ± 2 K) with variable scan speed (maximum scan time for each reflection: 60 s) by exploring the reciprocal space with $0 < h < 19, 0 < k < 19$ and $0 < l < 19$ and $\theta = 35°$. Following our experience for other minerals (PDCBG, PDG95a), we found that this limit to θ ensured sufficiently accurate results for our purposes. The diffracted intensities were corrected for Lorentz–polarization and background effects. After averaging the symmetry-related data, with an agreement of 1.6% based on F_o, 421 independent reflections were obtained. Of these, 201 with $I > 3\sigma(I)$ and $\theta > 15°$ were considered in the structure refinement (the latter limitation to reduce the effect of secondary extinction and also to avoid dependence on atomic charge as far as possible in the choice of scattering factors). Scattering factors for neutral atoms and anomalous dispersion corrections for scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The refinement of the structure was carried out by full-matrix least-squares, using the *SDP-Plus* package (B. A. Frenz & Associates, 1983), and minimizing the function $\Sigma w|F_o| - |F_c|)^2$. The final weights were assigned equal to $1/\sigma^2(F) = 4I/\sigma^2(I)$; the variance of each reflection $\sigma^2(I)$ was assigned according to the function $\sigma(F_o) = [\sigma^2(I) + (kI)^2]/2F_oLp$, where $\sigma(I)$ is the variance derived from counting statistics and k (= 0.03) is a coefficient for improving the goodness of fit. The atomic coordinates are reported in Table 2.* In the final difference synthesis, no peak exceeding 0.4 e Å^{-3} was found. The anisotropic a.d.p.'s are given in Table 5, together with their calculated estimates.

3. Procedure of calculation

In our previous lattice-dynamical works on the subject, whose principal scope was the calculation of thermal parameters of oxide and silicate minerals, we applied rigid-ion valence force-field (VFF) models first to forsterite α-Mg_2SiO_4 (PBG90) and then to beryllium and aluminium oxides such as BeO (bromellite), α-Al_2O_3 (corundum) and $BeAl_2O_4$ [chrysoberyl (PDG93; PDCBG)]. Following our interest in the matter, a similar procedure was adopted, essentially using Morse potentials instead of '6-exp' and fixed stretching constants: these potentials provided a better overall interpretation and they were first applied to quartz (PDG94) and, subsequently, to the whole olivine group (PDG95a). Here, besides the vibrational spectra, thermal

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* Lists of complete geometry, structure factors and calculated Raman- and IR-active frequencies have been deposited with the IUCr (Reference: CR0497). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

Crystal data

Chemical formula	$Ca_3Fe_2O_{12}Si_3$
Chemical formula weight	508.18
Cell setting	Cubic
Space group	$Ia\bar{3}d$
a (Å)	12.0643 (3)
V (Å^3)	1756
Z	8
D_x (Mg m^{-3})	3.844
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	25
θ range (°)	15.6–20.1
μ (mm^{-1})	5.50
Temperature (K)	293 (2)
Crystal form	Irregular fragment
Crystal size (mm)	0.15 × 0.15 × 0.10
Crystal color	Very pale green

Data collection

Diffractometer	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$
Absorption correction	Empirical; ψ scan (North, Phillips & Mathews, 1968)
T_{min}	0.90
T_{max}	1.00
No. of measured reflections	2174
No. of independent reflections	421
No. of observed reflections	201
Criterion for observed reflections	$I > 3\sigma(I)$
R_{int}	0.016
θ_{max} (°)	35
Range of h, k, l	$0 \rightarrow h \rightarrow 19$
	$0 \rightarrow k \rightarrow 19$
	$0 \rightarrow l \rightarrow 19$
No. of standard reflections	3
Frequency of standard reflections	Every 3 h
Intensity decay (%)	None

Refinement

Refinement on	F
R	0.011
wR	0.013
S	0.75
No. of reflections used in refinement	201
No. of parameters used	20
Weighting scheme	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$	0.01
$\Delta\rho_{max}$ (e Å^{-3})	0.4
$\Delta\rho_{min}$ (e Å^{-3})	−0.3
Extinction method	Secondary
Extinction coefficient	$g = 2.31$ (4) × 10^{-6}
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for andradite*

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^* a_j^* a_i.a_j.$$

	x	y	z	B_{eq}
Fe	0.0	0.0	0.0	0.3214 (8)
Ca	1/8	0.0	1/4	0.445 (2)
Si	0.375	0.0	1/4	0.283 (3)
O	0.03932 (2)	0.04863 (4)	0.65537 (4)	0.421 (6)

parameters (a.d.p.'s) and the values of thermodynamic functions at various temperatures were also satisfactorily accounted for, although the latter data were not considered in the fitting: in these papers, full details of our procedure of calculation are reported.

Table 3. *Empirical potential used*

		(1)	(2)	(3)	(4)			(1)	(2)	(3)	(4)
Atomic charge (electrons)†						Bending potentials (mdyn rad^{-2})					
Si		−1.566	−1.499		−1.418	O—Si—O	A	0.399	0.447		0.12569
Mg		−1.449	−1.514	−1.320	−1.482		B	0.033	0.058		−0.62573
Ca		−1.256	−1.465		−1.337		C				1.11716
Mn		−1.282	−1.370		−1.214	O−Al−O	A	0.245	0.056	0.062	0.48290
Fe^{2+}		−1.189			−1.097		B				0.65945
Fe^{3+}			−1.827		−1.805		C				0.04747
Al		−1.457	−1.511	−1.677	−1.286	O−Mg—O	A				0.16446
O		Calculated by difference with respect to the charge balance					B				−0.09038
							C				−0.31814
Stretching potentials						O—Ca—O	A				−0.05435
Si—O	A	2671.197	2471.496		2798.030	O—Mn—O	A				0.21503
	B	0.75610	0.77708		0.75624	O—Fe^{2+}—O	A				0.03889
	C	1.65054	1.64506		1.64173	O—Fe^{3+}—O	A				−0.20051
Mg—O	A	99.5203	184.083	142.8670	58.0805	Si—O—Si	A	0.121	0.143		0.13883
	B	1.47964	1.10797	1.15418	1.50304	Al—O—Al	A				0.12007
	C	2.17169	2.19544	2.28091	2.30494	Si—O—Al	A				0.18120
Ca—O	A	187.389	96.7239		126.2107						
	B	0.98372	1.29133		1.24017	Bending–stretching potentials (mdyn rad^{-1})					
	C	2.41138	2.47089		2.40593	O—Si—O/Si—O	A	−0.190	−0.168		0.10091
Mn—O	A	218.025	249.664		301.8444		B	0.012	−0.046		−0.05480
	B	0.88885	0.83920		0.66891	O—Al—O/Al—O	A	0.142	0.141	0.111	0.14044
	C	2.29810	2.32891		2.44907		B	−0.002	−0.002	−0.002	−0.00149
Fe^{2+}—O	A	131.087			73.7643						
	B	1.16470			1.48995	Stretching–stretching potentials (mdyn $Å^{-1}$)					
	C	2.19962			2.20857	Si—O/Si—O		0.276	0.204		0.11538
O···O	A	6.14300	6.30784		5.97077	AlO/Al—O		−0.059	0.002	−0.014	0.04744
(< 5.50 Å)	B	0.87475	0.85260		0.85146						
	C	3.68461	3.67217		3.67660						
Fe^{3+}—O	A		606.301		687.3882						
	B		0.79369		0.79374						
	C		2.07788		2.03413						
Al–O	A	375.338	518.788	498.881	264.3066						
	B	1.17960	1.13670	1.11933	1.37406						
	C	1.94723	1.88733	1.93587	1.90997						

For summations in the reciprocal lattice a maximum value of $d^*/2 = 0.85$ Å^{-1} has been assumed (Pilati, Bianchi & Gramaccioli, 1990a); in the direct lattice, bond distances and O···O contacts only are considered. Parameters A, B and C for Morse functions are given as: E(kJ mol^{-1}) $= A[e^{[-2B(r-C)]} - 2e^{[-B(r-C)]}]$, where r is the distance (Å). For potentials 1–3, and in all cases for angles (θ) not centred on Al, Mg or Si, constants K for bending and bending–stretching are given as: $K = A + B(\theta - 109.47°)$. For potential 4 and angles centred on Al, Si or Mg, the corresponding constants are: $K = A + B\cos(\theta) + C\cos^2(\theta)$. When B and/or C are not given, they are zero. Function 1. 29 parameters Morse force-field fitted to the vibrational frequencies of forsterite, FOR (including dispersion curves), fayalite, FAY, monticellite, MON, tephroite, TEP, and quartz, QUA (including dispersion curves, see PDG94), including Al (from best fit to the vibrational spectra of corundum COR). Function 2. 37 parameters Morse force-field fitted to vibrational frequencies of FOR (including dispersion curves), MON, TEP, QUA (including dispersion curves), pyrope, PYR, andradite, AND, and COR. Function 3. Derived from function 2, but assuming Mg to be different from Mg in the other substances. The constants relative to Al and Mg have been re-refined accordingly and all the remaining parameters are as for function 2. Function 4. Derived from best fit to QUA, FOR, MON, TEP, FAY, AND, COR, PYR, bromellite (BeO), chrysoberyl and andalusite (see PDG95b), a 69-parameter function. Here the parameters including beryllium are not reported, because they are not used. † Since the electron charge is negative, here negative numbers correspond to positive charges.

The constants in these empirical potentials were obtained by fitting the observed vibrational frequencies: for this purpose, the program VA04A (QCPE program No. 60: Powell, 1965) was employed. Most of the experimental data of the type used in the optimization process were derived from Raman and IR spectra, which are in general the only available information; in the few cases when they are reported in the literature, as for quartz and forsterite, the lowest branches of the phonon dispersion curves were also considered. Since the rigid-ion model is not fully adequate in reproducing the highest frequencies (whose contribution to the a.d.p.'s and thermodynamic functions is, however, negligible), an appropriate weighting (inversely proportional to the square) was assigned to the experimental data.

The potentials essentially derived from quartz and the olivine group (PDG95a) are reported as no. 1 in Table 3; to extend them to silicates containing Al, the optically active (Raman and IR) vibrational frequencies

of corundum (α-Al$_2$O$_3$) were also considered in the optimization.

More recently, a new set of potentials with 37 parameters was developed by fitting the data of all the above-mentioned minerals, except those containing beryllium (bromellite, chrysoberyl) and including pyrope (Mg$_3$Al$_2$Si$_3$O$_{12}$) and andradite (Ca$_3$Fe$_2$Si$_3$O$_{12}$). This potential is indicated as no. 2 in Table 3; a variant (no. 3 in Table 3) considers the eightfold-coordinate Mg atom in the pyrope structure to be different from the more usual sixfold, almost octahedrally coordinate Mg atom. In this variant, the parameters relative to the other atoms were left unmodified with respect to the no. 2 set, with the only exception of Al.

Still more recently, a new set of potentials was derived as an attempt to find a widely transferable potential (Pilati, Demartin & Gramaccioli, 1995b: hereinafter PDG95b) and is reported as no. 4 in Table 3. Herein, all the vibrational data concerning the whole

series of minerals mentioned above were included, plus andalusite (Al_2OSiO_4), a silicate containing both six- and fivefold-coordinate Al atoms. Owing to the considerable deformation of the oxygen polyhedron around the aluminium, a more complex bond-bending potential (of parabolic type) was introduced. This potential also accounts for the basic difference between an O—X—O angle of almost 180° and another O—X—O angle of almost 90°, as found in octahedra.

In deriving the last set of potentials bending constants of all metal-centred bond angles which had not been considered previously were also introduced, improving the general fit. In particular, this proved to be useful for the Mg atom to the point of suggesting the use of a more complex bending-potential scheme similar to that assumed for Al and Si.

This new set for almost any O—X—O angle includes both 1–3 non-bonded O···O interactions and bending constants. In a certain sense it is a kind of compromise, because of the considerable correlation between these parameters, and it virtually just indicates the importance of an angle between bonds which are partly covalent. For the minerals of the olivine group, no 1–3 O···O distance was common to two or more octahedral O—X—O angles and the corresponding interaction could be accounted for equally well, either considering the whole of it in terms of bond angle deformation or modification of the 1–3 distance. For garnets, however, the situation is more complex owing to the presence of different bond angles connecting the same 1–3 O atoms. Therefore, a straightforward comparison of 1–3 O···O distances only on the grounds of their magnitude was not advisable.

On introducing these interactions and bending constants at the same time, in a few cases the latter turned out to be negative: however, this result can be accepted in view of the cumulative contribution of the 1–3 interaction and the bending constant, which always corresponds to an increase in energy when bending takes place: the negative bending constant in practice corresponds to a weakening of the 1–3 interaction with respect to the average.

4. Discussion

The results are shown in Tables 4–6. Agreement with the experimental Raman and IR spectral data is especially good for the lower frequencies of andradite and grossular (usually, well within 10 cm^{-1}, with disagreement index $R = 3.6$ and 2.4%, respectively, using potential no. 4). This agreement is remarkable for grossular in particular, because no specific data for this mineral were included in the fit for deriving the potentials, which have been transferred as such from other substances. The interpretation of these spectra given by HFC is essentially confirmed; for andradite, a possible exception is an observed T_{1u} (TO) fundamental at 432.7 cm^{-1}, which

is ca 40 cm^{-1} lower than our calculations; the additional fundamental frequencies of 112, 704 and 1070 cm^{-1} reported by Madon et al. (1991) from IR powder data and used by these authors for deriving thermodynamic properties by Kieffer's method are not consistent with our model. For grossular, another T_{1u} (TO) fundamental around 540 cm^{-1} might be expected, unless that observed at 541.8 cm^{-1} is actually double; one of the three T_{2g} frequencies observed at 478, 509 and 577 cm^{-1} might not be fundamental, whereas an additional T_{2g} fundamental frequency around 667 cm^{-1} might be expected to occur. The 317 cm^{-1} E_g frequency is too low with respect to our calculations (344 cm^{-1}): the discrepancy is not excessive, but it is markedly higher than for most other observations.

For pyrope, the disagreement with the data reported by HFC is higher than for andradite and grossular, probably due to its particular situation (see below). Although there is evidence for some reassignments (indicated in Table 4), these cannot be considered yet as definitive. With respect to the only calculated values so far reported in the literature, the results obtained by Winkler et al. (1991) seem to give a better agreement (2.6%) with the experimental values than ours: however, only a few of the T_{1u} fundamental modes are reported by these authors. Therefore, a definite conclusion about the most successful model cannot be based on these limited grounds.

For almandine the disagreement with respect to the data reported by HFC is about as high as for pyrope, in line with a similar structural situation (see below). Therefore, also in this case there are no strong motives for reconsidering the interpretation of the vibrational spectra by HFC in detail. It seems, however, that the T_{1u} (TO) 111.5 cm^{-1} peak may be spurious; on the other hand, the presence of T_{2g} and E_g fundamentals at ca 138 and 275 cm^{-1}, respectively, might be expected in the Raman spectrum and a T_{1u} (TO) fundamental around 270 cm^{-1} might be expected to be present in the IR; similarly, the observed T_{1u} (TO) peak at 468 cm^{-1} does not seem too convincing.

For all the substances considered here, the agreement concerning the LO modes seems to be less satisfactory; however, in too many cases (marked with a question mark in Table 4) the experimental values are lower than the corresponding TO modes and for this reason no particular importance has been given to all the LO data.

Atomic displacement parameters (as U's) are reported in Table 5. Here also, the agreement with the experimental data for grossular and andradite is satisfactory, although the calculated values are somewhat lower than the corresponding observations. Since the calculated entropy for andradite (see later and Table 6) is slightly higher than the corresponding experimental result, rather than pointing out inconsistencies in our model, this would indicate the presence of systematic errors in the experimental data.

Table 4. *Vibrational spectra (cm⁻¹) at room temperature*

The calculated values correspond to the force field no. 4 in Table 3. The value of $R(= \Sigma|\text{freq}_{obs} - \text{freq}_{calc}|/\Sigma\text{freq}_{obs})$ is reported below for each column.

	Pyrope Obs	Pyrope Calc	Almandine Obs	Almandine Calc	Grossular Obs	Grossular Calc	Andradite Obs	Andradite Calc
T_{1u} (TO)	140	164	112		159	166	133	138
	200	206	138	142	186	190	152	161
	238		158	166	205	200	188	189
	260	256	196	179	245†	240	213	219
	279	278	236	220	302	301	246	245
	339	318	272		356	348	295	285
	365	370	318	291	399	400	305	297
	385	383	345	362	430	418	324	333
	400		376	396	449	442	350	349
	423	445	412	432	474	467	374	353
	458	465	448	458	505	517	433	475
	478	512	468	501		541	479	481
	536	543	525	533	542	549	505	499
	583	565	561	557	618	620	588	583
	664	631	635	604	843	878	795	856
	878	889	865	899	860	916	822	902
	906	937	889	944	914	931	876	911
	976	957	952	962				
T_{1u} (LO)	152	164	115		159	167	134	140
	218	209	147	143	189	192	154	161
	240		160	168	207	210	192	189
	263	257	205	185	249§	254	215	219
	280	300	246	230	303	302	247?	245
	353	319		273	357	353	332	336
	370	370	322	298	406	400	300?	285
	400	400	347	364	425?	418	322?	311
		404	396	398	530	448	359	353
	422?	453	422	437	468?	485	418	396
	556	557	518	518	503?	527	460	476
	474?	497	461?	473		544	487	496
	528?	526	534	538	579	579	532	541
	618	610	597	588	631	643	592	596
	667	642	638	616	883	887	858	865
	940	957	923	908	850?	931	819?	910
	889?	898	882?	962	1010	980	970	970
	1063	1015	1038	1004				
T_{2g}	208	175		138	178	177	176	179
	230	194	166	180	238	225	229	224
	272	263	198	202	246	244	235	228
	285		212	225	278	261	264	240
	318	320	293		330	334	311	306
	350	339	312	326	349	356	325	322
	379	374	355	354	383	391	382	352
		407		365	478	492	452	479
	490	481	474	459	509		494	491
	510	555	498		577‡	552	553	582
	598	648	576	537	629	631	593	622
	648	681	628	622		667	816	857
	866	893		652	826		842	906
	899	941	862	900	850	877	995	970
	1062	1029	892	948		920		
			1032	1020	1007	992		
E_g	203	210	163	170	178	176	173	173
	342	337		275	317	344	296	294
	365	376	326	346	369	371	352	330
	439	413	368	396	416	433	370	397
	524	559	421		526	554	494	508
	626	576	521	529	590	593	576	558
	911	868	593	554	852	831	843	817

Table 4 (cont.)

	Pyrope Obs	Pyrope Calc	Almandine Obs	Almandine Calc	Grossular Obs	Grossular Calc	Andradite Obs	Andradite Calc
	938	881	910	858	904	871	874	851
	920	891						
A_{1g}	362	355	347	343	374	382	370	373
	562	588	553	563	573	549	516	505
	925	936	910	920	881	889	872	855
R	0.039		0.039		0.024		0.036	

Observed data: HFC; the values (not symmetry labelled) reported by Gillet *et al.* (1992) almost match all these data, with only one exception (see below). The values observed for LO modes marked with a question mark are reported to be *lower* than the corresponding values observed for the TO modes. The value of the R index does not include the LO modes. † Values reported as a doublet, unconfirmed by our calculations. ‡ This frequency does not match any of the values reported by Gillet *et al.* (1992), who instead report a value of 549 cm⁻¹.

For pyrope and almandine, the situation is more complex and interesting, in line with the anomalous behaviour of the thermodynamic properties and with the experimental results obtained from X-ray diffraction (see *Introduction* and later). Here, at all temperatures the calculated U's are reasonably close to the corresponding experimental values, with the evident exception of the Mg^{2+} and Fe^{2+} atoms, whose unusually high experimental thermal displacements substantially exceed the theoretical estimate. Therefore, displacement parameters clearly indicate these atoms in particular to be involved in the process leading to unusual behaviour in thermodynamic properties.

A possible explanation for such disagreement in thermal displacements might consist of suggesting the potential of the eightfold coordinate Mg^{2+} (or Fe^{2+}) atom to be different from (weaker than) that of the corresponding, much more common, sixfold-coordinate counterpart and the motion to remain substantially harmonic. Accordingly, a potential for the eight-coordinate Mg atom was derived by fitting the pyrope vibrational data on this basis (see function 4 in Table 3); however, agreement with the experimental data was not essentially improved (see, for instance, Table 4). This situation seems to exclude a 'simple' harmonic model and would indicate rather the existence of disorder or strongly anharmonic motion. Moreover, as we have seen, the experimental a.d.p.'s can hardly be expressed in terms of second-rank tensors, as would happen instead if the motion were harmonic around a single position. Up to this point, our conclusion fully agrees with the results obtained by a number of qualified authors, who claim anharmonic vibrational behaviour for these atoms (Winkler *et al.*, 1991; GALJLA; AGL; GMS; Sawada, 1993).

Values of thermodynamic functions, such as entropy S and heat capacity at constant pressure Cp as a function of temperature are reported in Table 6. Since accurate

Table 5. *Atomic displacement parameters* $(\times 10^4)$

The numbers countersigning the calculated values correspond to the numbers of the force fields in Table 3. The temperature factor is in the form:
$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots\ldots + 2U_{23}klb^*c^*)]$.

			U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	B_{eq}
Andradite	Fe	Obs	41 (1)	−1 (1)	U_{12}	U_{11}	U_{12}	U_{11}	0.32
(293 K)		Calc (4)	34	−1					0.27
	Ca	Obs	39 (1)	0	0	65 (1)	13 (1)	U_{22}	0.45
		Calc (4)	37			53	7		0.37
	Si	Obs	34 (1)	0	0	37 (1)	0	U_{22}	0.28
		Calc (4)	34			33			0.26
	O	Obs	53 (1)	4 (2)	−7 (1)	61 (1)	1 (2)	46 (1)	0.42
		Calc (4)	49	2	−6	53	3	42	0.38
Grossular	Al	Obs	38 (1)	−1 (1)					0.30
(293 K)		Calc (4)	31	0					0.24
	Ca	Obs	34 (1)			56 (1)	9 (1)		0.39
		Calc (4)	32			52	7		0.36
	Si	Obs	30 (1)			34 (1)			0.26
		Calc (4)	29			28			0.22
	O	Obs	48 (1)	1 (1)	−6 (1)	52 (3)	4 (1)	40 (1)	0.37
		Calc (4)	40	1	−4	44	1	34	0.31
Pyrope	Al	Obs	21 (1)	0 (1)					0.17
(100 K)		Calc (4)	19	0					0.15
	Mg	Obs	27 (1)			51 (1)	12 (1)		0.34
		Calc (4)	23	3		28	4		0.22
	Si	Obs	17 (1)			19 (1)			0.15
		Calc (4)	17			17			0.13
	O	Obs	31 (1)	4 (1)	6 (1)	37 (1)	0 (1)	25 (1)	0.25
		Calc (4)	28	3	−4	31	0	23	0.22
Pyrope	Al	Obs	31 (1)	0 (1)					0.25
(293 K)		Calc (1)	26	0					0.21
		Calc (2)	32	−1					0.25
		Calc (3)	34	−1					0.27
		Calc (4)	30	−1					0.24
	Mg	Obs	45 (1)			104 (2)	31 (1)		0.67
		Calc (1)	34			68	17		0.45
		Calc (2)	34			52	9		0.36
		Calc (3)	38			54	6		0.38
		Calc (4)	35			50	9		0.35
	Si	Obs	25 (1)			30 (1)			0.22
		Calc (1)	24			29			0.21
		Calc (2)	31			27			0.22
		Calc (3)	34			28			0.24
		Calc (4)	29			28			0.23
	O	Obs	48 (1)	9 (1)	−11 (1)	59 (1)	−2 (1)	36 (1)	0.38
		Calc (1)	39	3	−6	49	2	39	0.33
		Calc (2)	46	4	−8	51	−3	34	0.34
		Calc (3)	48	3	−6	51	−2	36	0.35
		Calc (4)	43	5	−7	49	−3	36	0.34
Almandine	Al		15 (1)	1 (1)					0.12
(100 K)			19	0					0.15
	Fe	Obs	17 (1)			34 (1)	3 (1)		0.22
		Calc (4)	13			24	2		0.16
	Si	Obs	12 (1)			14 (1)			0.11
		Calc (4)	18			16			0.14
	O	Obs	28 (1)	6 (1)	−7 (1)	32 (1)	0 (1)	24 (1)	0.22
		Calc (4)	29	3	−4	31	0	23	0.22
Almandine	Al	Obs	27 (1)	1 (1)					0.21
(293 K)		Calc (4)	31	0					0.24
	Fe	Obs	35 (1)			75 (1)	9 (1)		0.49
		Calc (4)	26			54	6		0.35
	Si	Obs	17 (1)			24 (1)			0.17
		Calc (4)	31			28			0.23

Table 5 (cont.)

			U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	B_{eq}
	O	Obs	42 (1)	13 (1)	−13 (1)	57 (1)	−4 (1)	33 (1)	0.35
		Calc (4)	45	5	−8	50	−2	36	0.35
Almandine	Al	Obs	36 (1)	1 (1)					0.28
(420 K)		Calc (4)	41	0					0.32
	Fe	Obs	41 (1)			109 (1)	13 (1)		0.68
		Calc (4)	49			77	10		0.53
	Si	Obs	24 (1)			35 (1)			0.25
		Calc (4)	42			38			0.31
	O	Obs	59 (1)	12 (1)	−16 (1)	76 (1)	−2 (1)	44 (1)	0.47
		Calc (4)	60	7	−10	67	−3	46	0.45
Almandine	Al	Obs	45 (1)	1 (1)					0.36
(500 K)		Calc (4)	48	0					0.38
	Fe	Obs	52 (1)			133 (1)	15 (1)		0.84
		Calc (4)	59			93	12		0.64
	Si	Obs	33 (1)			43 (1)			0.31
		Calc (4)	50			45			0.37
	O	Obs	66 (1)	14 (1)	−18 (1)	94 (1)	−2 (1)	53 (1)	0.56
		Calc (4)	70	8	−12	78	−3	53	0.53

For all the stuctures reported here, the a.d.p.'s are relative to the atoms corresponding to the list in Table 2. All the symmetry constraints concerning the U_{ij}'s are reported only for andradite. Observed data for pyrope and almandine from AGL and GALJLA, for grossular from Ungaretti (1994); our own data for andradite. A minimum estimate of 1 in the last digit for the standard deviation has been assumed, although in several cases the reported values are sensibly smaller. For essentially pure andradite, see also: Novak & Gibbs (1971) and Hazen & Finger (1989). For pyrope, see also: Novak & Gibbs (1971) and Hazen & Finger (1989).

crystal structure data at different temperatures correspond only to those reported in Table 5, and are largely insufficient for our purposes, as a starting point for our calculations the unit-cell parameters and atomic coordinates of the nearest structure to the temperature of interest have been used here.

For grossular, the calculated values for the specific heat Cp and entropy at room temperature are lower than the corresponding experimental values (ca 2.7 and 3.8%, respectively). However, the measured values on a synthetic and a natural sample differ (Westrum et al., 1979; Haselton & Westrum, 1980, respectively) and our values are in much better agreement with those of the natural sample. At very low temperature, around 10 K, the observed specific heat is significantly larger than the corresponding calculated value. As for other minerals where iron is present as an impurity, such as for instance some pyroxenes (Krupka, Robie, Hemingway, Kerrick & Ito, 1985), this difference between the calculated and the observed Cp's might be due to a Schottky-type contribution (Gopal, 1966) arising from a small amount of impurities (e.g. Fe) in solid solution. Such a possibility is supported by the difference observed in the same range of temperature between the observed values relative to the synthetic and natural sample. On examining Table 6, the Schottky-type contribution to entropy can be noticed to amount to ~ 2 J mol⁻¹ K⁻¹). This contribution should be subtracted from the experimental values at all temperatures above 20 K, before comparison with the calculated data and on these grounds the agreement could still be significantly improved. Similar phenomena might also occur for the other garnets, but the effects

are less clear due to the contemporary presence of order–disorder transitions (see below).

For almandine, a contribution of $3R\ln 5$ (corresponding to complete magnetic disorder for the Fe^{2+} atom) was added to the vibrational estimate of entropy above 20 K, in agreement with the antiferromagnetic behaviour with a λ transition occurring at the Néel temperature of 8.7 K (Metz et al., 1983; Anovitz et al., 1993); similarly, a contribution of $2R\ln 6$ was considered above 80 K for andradite, where the Néel temperature is 11.5 K and the antiferromagnetic behaviour concerns the Fe^{3+} atom (Murad, 1984). On examining the experimental data reported in Table 6, there is no question that around 150 K complete magnetic disorder is essentially achieved for both minerals. This is in agreement with most authors, for instance AGL or Armbruster, Geiger, Amthauer, Lottermoser & Lager (1991), who claim that since these transition temperatures are very low, almost complete magnetic disorder should be expected to occur even at 100 K.

For andradite in particular, our results above 140 K are in fairly good agreement with the experimental values obtained by Robie et al. (1987). For instance, the calculated values for Cp and S at 298 K agree with the corresponding experimental results within 2.0 and 1.6%, respectively. Especially at high temperature (> 400 K), some disagreement could be due to neglecting the anharmonic contribution, or also in part to the electronic contribution, a point which might be of some importance with phases containing transition elements (see, for instance, fayalite, Fe_2SiO_4, in PDG95a, or also below). Instead, at low temperature, as we have seen,

the discrepancy between the observed and calculated values is clearly due to the influence of the magnetic contribution: for instance, at 10 K, *i.e.* in close proximity to the Néel temperature, the observed specific heat is much higher than the calculated vibrational value and this discrepancy continues on raising the temperature, until (around 140 K) almost complete magnetic disorder is reached. The trend for entropy of course corresponds to the trend in Cps: from Table 5, it is clear that the additional contribution of $2R\ln 6$ at 80 K is too high to assume virtually complete magnetic disorder, whereas at higher temperatures this assumption agrees with the experimental behaviour.

In spite of all this, some authors, such as Madon *et al.* (1991) or Gillet, Le Cléac'h & Madon (1990), consider the magnetic contribution for andradite to remain constant above 20 K, where it is only 58% of the value corresponding to complete disorder. Clear reasons for this assertion are not given, apart from that of obtaining an excellent agreement (within less than 1%) with the experimental data, using Kieffer's method.

For pyrope, the situation is different from andradite and grossular, in line with the disagreement observed in the thermal parameters. For this substance, the experimental values for entropy at all temperatures are substantially higher than the corresponding vibrational estimates: for instance, at room temperature (298 K) our estimate for S is 237.2 J mol^{-1} K^{-1} against an experimental value of 266.3 J mol^{-1} K^{-1}. This result is in close agreement with Winkler *et al.*'s (1991) calculations, who claim anharmonicity to be responsible for this behaviour. For almandine, a similar situation is encountered, if the magnetic contribution is accounted for.

With respect to specific heat Cp, our calculated value for pyrope at room temperature and above shows a reasonable agreement (within 2%) with the experimental value, in spite of the notable differences observed for entropy and thermal parameters, whereas at 100 K the difference between the experimental and calculated values is high. However, at very low temperature (<15 K), the calculated values of thermodynamic functions are again in good agreement with the vibrational estimates and no residual entropy is observed at 0 K, in contrast to other substances, *e.g.* ice. This result agrees with previous observations by several authors (see *Introduction*): for instance, Hofmeister & Chopelas (1991*b*) observe that 'from *ca* 50 to 150 K, the measured heat capacity is significantly in excess of the theory'. Such behaviour might suggest a process of disordering to occur in this interval of temperature, *i.e.* a type of transition should occur between an ordered (stable at very low temperature) and a disordered phase, stable at higher temperature. For almandine, the situation, although similar, is more complex due to the simultaneous occurrence of the magnetic transition and for this reason the trend in the specific heat at low temperature is less clear, since it includes contributions from both these effects.

Table 6. *Values of thermodynamic functions* $(J\,mol^{-1}\,K^{-1})$

T (K)	S_{obs}	S_{calc}	Cp_{obs}	Cp_{calc}
Pyrope†				
5	0.00	0.00	0.00	0.00
10	0.01	0.01	0.04	0.03
15	0.05	0.04	0.24	0.16
20	0.20	0.12	0.86	0.46
30	1.08	0.54	4.25	1.97
40	3.15	1.53	11.05	5.56
50	6.6	3.4	21.1	11.9
60	11.6	6.3	33.6	21.1
70	17.8	10.4	47.6	32.8
80	25.1	15.6	62.7	46.2
100	42.5	27.7	94.3	76.7
120	62.5	44.5	126.0	109.6
140	84.2	63.8	156.8	141.0
160	107.1	84.4	185.7	170.9
180	130.5	106.4	212.0	198.6
200	154.1	163.2	235.8	223.8
220	177.6	185.6	257.5	246.9
240	200.9	208.1	277.2	267.9
260	223.8	230.3	295.3	287.1
280	244.3	252.3	311.7	304.3
298	266.3	271.7	325.3	318.6
350	321.2	325.8	360.2	353.3
400	371.0	374.7	385.8	379.4
500	458.0	463.6	422.8	417.2
600	545.0	541.7	443.5	442.5
Almandine‡				
10	23.79	0.01	16.25	0.05
15	30.13	0.06	15.02	0.26
20	34.34	0.20	14.35	0.80
30	40.38	41.15	16.59	4.07
40	46.15	43.22	24.75	11.54
50	52.9	46.9	36.4	22.8
60	60.7	52.2	50.1	36.8
70	69.5	59.2	64.9	52.2
80	79.2	67.1	80.4	68.6
100	100.5	85.8	112.1	102.2
120	123.8	107.3	143.6	134.6
140	148.2	130.4	173.8	165.3
160	173.3	154.3	202.0	193.7
180	198.6	178.6	227.9	219.7
200	223.8	199.8	251.5	243.5
220	248.8	224.0	273.2	265.1
240	273.5	248.0	293.5	284.7
260	297.7	307.0	312.3	303.1
280	321.5	330.1	329.2	319.1
293	336.8	344.8	339.0	328.8
298	342.6	350.4	342.8	332.3
325	373.0	380.1	361.5	350.1
350	400.4	406.5	374.7	364.6
400	451.8	455.0	397.6	389.1
420	471.0	475.0	404.9	397.1
500	544.3	546.1	430.9	424.0
600	625.1	625.6	454.7	446.8
700	696.5	695.6	472.6	462.5
800	760.6	758.4	486.0	473.0
1000	871.0	865.8	501.5	489.1
Andradite§				
5	0.14	0.00	0.50	0.00
10	4.35	0.02	28.90	0.15
15	13.90	0.09	8.22	0.46
20	15.60	0.26	4.74	1.13
30	17.59	1.15	6.16	4.42
40	20.25	3.21	13.51	11.55

Table 6 (cont.)

T (K)	S_{obs}	S_{calc}	Cp_{obs}	Cp_{calc}
50	24.4	6.9	24.6	22.9
60	30.1	11.6	39.1	37.6
70	37.4	18.7	55.8	54.5
80	46.0	27.1	73.6	72.7
100	66.4	75.0	110.4	110.1
140	114.8	123.2	180.0	178.4
180	167.2	175.3	237.6	234.2
200	193.6	201.1	262.3	258.0
220	219.6	226.8	284.2	279.4
240	245.2	252.0	304.0	298.5
280	294.7	300.6	338.2	331.4
298	316.4	321.7	351.9	344.1
400	428.2	431.1	404.9	397.8
500	522.8	523.6	441.0	430.8
600	605.2	604.0	464.0	452.6
700	677.9	674.7	480.3	468.1
800	742.6	737.7	490.2	476.5
900	800.8	794.4	498.4	484.7
1000	853.7	845.8	504.2	491.5

T (K) Grossular	S_{obs} Synth.	Natur.	S_{calc}	Cp_{obs} Synth.	Natur.	Cp_{calc}
10	0.03	0.14	0.01	0.07	0.29	0.04
20	0.24	0.49	0.14	1.29	0.93	0.55
40	2.47	2.79	1.96	8.29	8.28	7.33
60	9.2	9.3	8.1	27.9	27.0	26.4
80	20.9	20.7	19.3	55.8	54.6	54.0
100	36.7	34.2	33.1	87.7	86.1	85.4
150	87.9	86.6	82.9	169.0	167.3	163.4
200	146.2	141.9	139.5	237.1	236.2	229.5
250	205.1	203.1	196.8	291.1	290.5	282.7
298	260.1	255.1	250.1	333.2	331.0	322.9
350	316.5	313.9	305.0	370.3	363.0	356.9
400	366.0	361.0	354.4	396.8	389.7	382.5
500	457.3	451.7	444.1	429.7	425.7	418.9
600	537.4	531.3	522.7	451.6	449.7	443.3
700	608.0	601.4	592.3	462.8		457.5
800	670.9	664.1	654.3	469.3		469.4
900	727.4	721.1	710.4	484.0		478.5
1000	778.8	772.2	761.5	498.0		486.1
1200	870.2		851.6			498.4

All the calculated values in the table were obtained using the potential no. 4 in Table 3; the $(Cp - Cv)$ differences were calculated using the volume thermal expansion α, the bulk modulus K_t and their derivatives $d\alpha/dT$ and dK_t/dT, reported by Madon et al. (1991), Anowitz et al. (1993) or by Hofmeister & Chopelas (1991b); due to the lack of experimental measurements below 100 K, for each garnet a constant value for K_t and a linear extrapolation for α to a zero value at 0 K were assumed. For almandine, interpolation of the unit-cell volumes reported by GALJLA provides a value of $d\alpha/dT$, which is clearly too high (about four times as for the other garnets) and therefore for this substance average values of α and K_t were used for the whole range 100–1000 K. For andradite, a value of dK_t/dT equal to that of grossular was also assumed (-0.024 GPa K^{-1}), in line with the observed similarity of this property for all garnets. The crystal data used in our calculations correspond to those at room temperature obtained by Ungaretti (1994) for grossular and by us for andradite, respectively, and to those reported by AGL and GALJLA for pyrope and almandine at the corresponding temperatures; for all the other temperatures, due to the lack of experimental measurements the crystal data at the nearest temperature were used. Experimental values of Cp and S for pyrope from Haselton & Westrum (1980) and above 400 K from Tequi et al. (1991); for almandine from Anovitz et al. (1993); for grossular from Haselton & Westrum (1980) on a synthetic sample, from Westrum et al. (1979) on a natural sample and from Krupka, Robie & Hemingway (1979) above

350 K; for andradite from Robie et al. (1987). For all the substances considered here, above 80 K the calculated values of entropy were corrected for the effect of thermal expansion by adding

$$\int_{T_0}^{T} (Cp - Cv)/T \, dT,$$

where T_0 is the temperature at which the corresponding crystal data were obtained and used in our calculations. † Values of S_{calc} above 180 K include the contribution of 34.5 J mol^{-1} K^{-1} due to disorder of the Mg atom (see text). ‡ Values of S_{calc} above 20 K include the magnetic contribution of $3R\ln5$ ($= 40.14$ J mol^{-1} K^{-1}); the values above 240 K also include the additional contribution of 34.5 J mol^{-1} K^{-1} due to disorder of the Fe atom (see text). § Values of S_{calc} above 80 K include the magnetic contribution of $2R\ln6$.

If the Mg (or the Fe) atom is assumed to have achieved complete static disorder at higher temperature, by shifting out of its (24c) special position at $(0,\frac{1}{4},\frac{1}{8})$ in the $Ia3d$ space group to be statistically distributed over four different sites in conformity with a general position, the increase in entropy due to this transition can be evaluated, for instance, on applying the following formula derived from simple statistical considerations (Ulbrich & Waldbaum, 1976)

$$S = -Rm/Z\Sigma P_i \ln P_i, \tag{1}$$

where P_i is the probability of finding the Mg atom at the ith site, m is the site multiplicity and Z is the number of formula units per cell.

Application of the above ideas and formula to our case leads to an additional entropy contribution of 34.5 J mol^{-1}K^{-1} for both pyrope and almandine. It is interesting to notice that for these substances just by adding this 'static disorder' contribution our final calculated values at room temperature and higher become close to the experimental results (see Table 6): therefore, the existence of extensive anharmonic motion or 'dynamic' disorder, as claimed by most authors for both these minerals to explain their 'anomalous' behaviour, cannot be considered yet as definitely proved. Even the asymmetry observed in the Mössbauer spectrum for the Fe^{2+} atom in almandine (see Introduction) might indicate that the site is not the (24c) fully symmetric one, in agreement with our considerations. Curiously enough, Hofmeister & Chopelas (1991b), who first advanced the possibility of having static disorder in pyrope and of using Ulbrich and Waldbaum's formula for evaluating the additional entropy, rejected the idea almost immediately, since the contribution was not consistent with their own results based on Kieffer's model.

Another proof in favour of the existence of 'static' disorder instead of substantial anharmonic behaviour for both pyrope and almandine is the following: if the harmonic model is basically wrong and the 34.5 J mol^{-1} K^{-1} difference results by mere chance, then it is difficult to

admit that, besides interpreting the vibrational spectra satisfactorily, the model provides a density of states which can be successfully used to reproduce the specific heat for a whole range of high temperatures. This agreement is even more surprising, since anharmonicity should become more evident when thermal displacement is increased.

On the other hand, as a result of clear experimental evidence obtained by GALJLA for almandine, on increasing temperature, the mean-square-displacement amplitude and anisotropy of the Fe^{2+} atom increase much more than that of the other atoms (in particular, the O atom). Moreover, the ΔU observed along the 'short' Fe—O distance of 2.22 Å does not show extensive variation with temperature, whereas along the 'longer' Fe—O distance of 2.36–2.38 Å there is a distinct temperature dependence: all such phenomena are considered by these authors as substantial proof in favour of 'dynamic' disorder.

However, what seems to be certain is that along the connecting Fe···O directions ('bonds') the situation is certainly quite different from other 'true' bonds, such as Al—O or Si—O, or the corresponding metal–oxygen bonds in grossular and andradite, which are definitely more rigid. Even in our model, a strong temperature dependence can be accounted for, since the disordered sites coalesce at low temperature: for instance, near 0 K thermodynamic data clearly indicate the Mg^{2+} or Fe^{2+} atoms to be in an energy minimum, with no disorder, which should correspond to the $(24c)$ special position according to the only possible interpretation; on increasing temperature, disorder begins to occur (even at 20 K) until it reaches the maximum value at ca 300 K. Therefore, since disorder increases with temperature, there should be a substantial increase of the a.d.p.'s, as a consequence of a transition from a 'normal' situation around the main energy minimum, probably accounted for by a second-rank tensor, to an overlap of several distributions around the various disordered sites. Unfortunately, our potentials are not yet reliable enough to account for energy minima of lesser importance and for this reason our calculations have not been extended to find the exact location of the disordered sites, as a first step to evaluate the mean-square displacement around the 'central' $(24c)$ position.

At higher temperatures, where no transition is involved, the mean-square displacement of the Fe atom still increases considerably more than that of the O atom: for instance, on going from 100 to 500 K, the ratio between the observed corresponding B_{cq}'s at 500 and 100 K, respectively, is 0.56/0.22 = 2.55 for the O atom and 0.84/0.22 = 3.82 for the Fe atom. On these grounds, however, there is not substantial disagreement even with the corresponding ratios between the B_{cq}'s obtained from our harmonic calculations (0.53/0.22 = 2.41 and 0.64/0.17 = 3.77 for the two atoms, respectively): these same ratios are also virtually maintained in the

components of the U's, accounting for a similar trend in anisotropy. Therefore, in contrast to widespread belief, a substantial increase of thermal parameters and/or anisotropy of one atom with respect to those of the others on raising temperature is not necessarily proof of disorder or anharmonic motion.

A similar result can be obtained on considering the corresponding differences ΔU in the mean-square vibrational parameters along the Fe–O bonding vectors: for instance, according to GALJLA, along the shorter Fe—O bond on going from 100 to 500 K they vary from -17 to -11 (1) $\times 10^{-4}$, $i.e.$ they are considerably different. However, these differences might just indicate the absence of rigid-body vibrational behaviour, which is not implied even in our model.

For all these reasons, since our simple harmonic rigid-ion model and our potentials satisfactorily account for most vibrational and thermodynamic properties of all the garnets investigated so far here, we believe that more specific reasons and detailed evidence should be provided in favour of any other model involving greater complexity. It would be very interesting if thermal parameters could also be measured at very low temperatures (below 100 K) and especially in proximity of the order–disorder transitions.

In any case, since the borderline between static and dynamic disorder is not so clearly defined and the two phenomena are usually combined together, the situation for pyrope and almandine might be reasonably explained by implying a harmonic motion for small displacements around the 'disordered' sites and anharmonic motion for atoms 'jumping' from one position to another. Since the latter implies the higher energy levels only, if temperature is not too high the values of thermodynamic functions essentially depend on a harmonic pattern as our scheme of calculations: all this, of course, provided the frequencies do not vary extensively on shifting the atoms from their average position and thereby do not lead to substantial change in the density of states. On such a basis, our point of view might actually be reconciled with that of other authors, who might just imply disorder to be always essentially 'dynamic'.

For almandine in particular, apart from what has already been specified, at room temperature the specific heat value derived from our calculations is not fully satisfactory, although, as we have seen, for entropy the additional contribution for a disordered structure would bring our calculated result in line with the experimental data (within 2.3%). This might indicate that a situation of complete disorder is not achieved or it is reached only at substantially higher temperatures than 298 K, in keeping with the larger size of the Fe^{2+} atom with respect to Mg^{2+}; in addition, the consequences of using a less satisfactory potential for this substance (see above) should not be underestimated. Another possible source of complexity in deriving thermodynamic properties is linked to the presence of a transition element such as

Fe: in this case, additional factors might contribute to entropy, as for instance a Schottky thermal contribution arising from disordering the iron $3d$-electrons, which might amount to a maximum value of $3R\ln 2$ (Metz *et al.*, 1983; Anovitz *et al.*, 1993); a similar situation might also arise at high T for andradite.

In conclusion, the use of empirical potentials seems to be extremely interesting in reproducing thermal parameters and thermodynamic functions of minerals and inorganic substances at different temperatures, and the calculations are reliable, at least where the harmonic model holds, affording more reasonable results than other widely used methods, such as Kieffer's, which are considerably more approximate. For crystals showing anharmonic behaviour or disorder, these calculations at least in some cases seem to point out quite well where the inconveniences are and provide interesting explanations, especially if information on thermal parameters is used together with the comparison of estimates of different thermodynamic functions.

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