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2005 J. Phys.: Condens. Matter 17 277

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Low temperature Raman spectroscopic study of scandium molybdate

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Received 28 October 2004, in final form 28 October 2004

Published 20 December 2004

Online at stacks.iop.org/JPhysCM/17/277

Abstract

Low temperature Raman spectroscopic measurements are carried out on $\text{Sc}_2(\text{MoO}_4)_3$ to probe the orthorhombic–monoclinic phase transition. Phonon frequencies and their temperature coefficients are found to change discontinuously across the transition. Several modes are found to disappear while some new modes appear across the transition. The evolution of intensities of the modes suggests a two-phase coexistence over a temperature interval of about 20 K both in the cooling and heating cycles. The transition is found to occur at 142 ± 10 K upon cooling while the reverse transition occurs at 174 ± 11 K during the heating cycle, i.e., the system exhibits a hysteresis of 32 K. In contrast to the usual behaviour, most of the phonon modes in the monoclinic phase exhibit softening upon further cooling. Separation of the temperature dependence of Raman mode frequencies into quasi-harmonic and purely anharmonic contributions using reported high pressure Raman data reveals that bending modes of MoO_4 ions are the most anharmonic among the modes studied.

1. Introduction

Reports of high and isotropic negative thermal expansion (NTE) over a wide range of temperatures in $\text{Zr}(\text{WO}_4)_2$ [1] have generated considerable interest in such materials with framework structure and substantial empty space. Pressure and temperature dependent Raman spectroscopic studies [2–4] have provided valuable insight into the nature of NTE in $\text{Zr}(\text{WO}_4)_2$, identifying phonons that exhibit large anharmonicity. In addition to the librational rigid unit mode, several other lattice and bending modes have been found to have significantly large anharmonicity [4]. Following the discovery of large NTE in $\text{Zr}(\text{WO}_4)_2$, a number of other molybdates and similar framework structures are being studied. NTE in the $\text{A}_2(\text{MO}_4)_3$ ($\text{A} = \text{Sc}, \text{In}; \text{M} = \text{Mo}, \text{W}$) family was recently reported by Evans *et al* [5]. Many compounds of this family are known to undergo a phase transition from a high temperature orthorhombic to a low temperature monoclinic structure as temperature is reduced below the transition temperature [6]. The transition temperatures vary widely, and this has been related to the

electronegativity of the A^{3+} cation [5]. The low temperature phase has a positive thermal expansion whereas the high temperature orthorhombic phase often exhibits a negative thermal expansion coefficient. However, the orthorhombic phase of $\text{In}_2(\text{WO}_4)_3$ ($T_C = 523$ K) was recently reported to exhibit a small positive thermal expansion [7].

We have carried out Raman spectroscopic studies of $\text{Sc}_2(\text{MoO}_4)_3$ as a function of temperature to study the monoclinic–orthorhombic transition both in the heating and cooling cycles. At ambient temperature $\text{Sc}_2(\text{MoO}_4)_3$ is orthorhombic. Extensive x-ray and neutron diffraction measurements carried out in the heating cycle have revealed that the structure is monoclinic below 178 K and exhibits positive thermal expansion [8]. Above this temperature it undergoes a displacive phase transition to an orthorhombic structure with a volume expansion of 1.4%. An orthorhombic phase that has an average NTE of $-6.3 \times 10^{-6} \text{ K}^{-1}$ persists up to 1053 K.

Monoclinic $\text{Sc}_2(\text{MoO}_4)_3$ belongs to the space group $P2_1/a$ [8]. It contains six MoO_4 tetrahedra corner-linked with four ScO_6 octahedra. Unlike in the cubic $\text{Zr}(\text{WO}_4)_2$ structure, there are no terminal oxygen atoms in $\text{Sc}_2(\text{MoO}_4)_3$. For $\text{Zr}(\text{WO}_4)_2$, the transverse motion of terminal oxygen atoms has been envisaged to lead to rotational/librational motion of WO_4 rigid units, and the coupled rotation of ZrO_6 units to lead to a net reduction in the volume of the structure as temperature is increased [1, 9]. On the other hand, on the basis of structural data across the monoclinic–orthorhombic transition in $\text{Sc}_2(\text{MoO}_4)_3$, it has been speculated [8] that the phonons responsible for NTE in the orthorhombic phase are related to those frozen out across the phase transition. However, there is no report of anharmonicity of the various phonon modes in this material. Recent high pressure Raman spectroscopic studies of molybdate internal modes [10, 11] have revealed softening of symmetric and antisymmetric stretching modes. However, lattice modes were not studied. In view of this it is of interest to identify the phonons with large anharmonicities and evaluate their contributions to the thermal expansion of $\text{Sc}_2(\text{MoO}_4)_3$. We also examine the contribution of the various phonon modes to thermal expansion in $\text{Sc}_2(\text{MoO}_4)_3$ in comparison with those of $\text{Zr}(\text{WO}_4)_2$.

Raman spectroscopic investigations of the orthorhombic–monoclinic phase transition in $\text{Sc}_2(\text{MoO}_4)_3$ are carried out as a function of temperature in the range 10–300 K. The spectra are analysed to obtain the temperature dependences of mode frequencies. Using the reported high pressure Raman data, the ‘quasi-harmonic’ and ‘true anharmonic’ contributions to thermal expansion are separated. The changes in anharmonicities of the different phonons across the transition are discussed in the context of thermal expansion behaviour. Hysteresis of the phase transition is also examined.

2. Experimental details

A single-phase polycrystalline $\text{Sc}_2(\text{MoO}_4)_3$ sample was prepared by Mary by a conventional solid-state technique from stoichiometric quantities of Sc_2O_3 and MoO_3 [8]. Raman spectra were recorded in the back-scattering geometry using 200 mW of power of the 488 nm line from an Ar ion laser. Scattered light was analysed using a double monochromator (SPEX 14018) and detected using a photomultiplier tube (Hamamatsu R943-02) operating in the photon counting mode. Sample powder was pressed onto the greased cold head of a helium closed-cycle refrigerator and spectra were recorded from 10 K up to room temperature at intervals of 20 K, and at closer intervals around the phase transition temperature. Measurements were also made during the cooling cycle. Close to the phase transition temperature the heating/cooling rate was carefully controlled to avoid overshooting into the orthorhombic/monoclinic phase. The spectra were fitted to Lorentzian line shapes to determine the central frequency and width. Polarized Raman measurements, when made on oriented single crystals, yield information

on the elements of the polarizability tensor and the symmetry of the phonons. On the other hand, measurements on polycrystalline samples using plane and circularly polarized light can in principle be used for obtaining only the polarizability invariants such as the isotropic part z^2 and the symmetric anisotropy γ_s^2 [12]. As the aim of the present study is to probe the changes in the phonon spectrum across the structural phase transition and to identify the phonons with large anharmonicity in the context of negative thermal expansion, we made only unpolarized measurements on the polycrystalline samples.

3. Results and discussion

The low temperature monoclinic phase of $\text{Sc}_2(\text{MoO}_4)_3$ has eight formula units per unit cell (space group $P2_1/a$) that result in 408 vibrational degrees of freedom. Factor group analysis of isostructural $\text{In}_2(\text{WO}_4)_2$ has been reported recently [7]. The point group symmetry (C_{2h}) permits only singly degenerate irreducible representations. The distribution of phonon modes is: $102A_g + 102B_g + 102A_u + 102B_u$, out of which A_g and B_g are Raman active. On the other hand, the high temperature orthorhombic phase has only four formula units per unit cell (space group $Pnca$) and consequently the vibrational degrees of freedom number only 204. Here also group theory predicts all modes to be non-degenerate. The irreducible representations associated with the Raman and IR active phonons are $25A_g + 26B_{1g} + 25B_{2g} + 26B_{3g}$ and $25A_u + 26B_{1u} + 25B_{2u} + 26B_{3u}$ respectively.

Figure 1 shows the Raman spectrum of scandium molybdate at 10 K. A total of 31 distinct Raman modes could be identified in the frequency range $50\text{--}1100\text{ cm}^{-1}$. Table 1 lists the frequencies of the observed Raman modes in the monoclinic phase. One can see several weak peaks/shoulders in addition to those labelled as 1–31 in figure 1. These weak peaks/shoulders could not be systematically followed as a function of temperature due to statistical fluctuations of intensity. Hence these are not listed in table 1. However, these could also be genuine Raman modes. The observation of fewer of modes than predicted could be either due to accidental degeneracy of phonon frequencies or due to insufficient intensities arising from small polarizabilities of several modes. As in other NTE systems with similar framework structure, no modes could be observed between 450 and 750 cm^{-1} . Lattice, translational and librational modes appear in the range $50\text{--}300\text{ cm}^{-1}$. One can see from table 1 that the lowest frequency mode in $\text{Sc}_2(\text{MoO}_4)_2$ appears at 80 cm^{-1} . This may be compared with that in $\text{Zr}(\text{WO}_4)_2$ where the lowest Raman mode is the WO_4 rigid unit librational mode at 41 cm^{-1} . Comparing mode frequencies in $\text{Sc}_2(\text{MoO}_4)_3$ and $\text{Zr}(\text{WO}_4)_2$, no modes are expected below 41 cm^{-1} since both Sc and MoO_4 are lighter than Zr and WO_4 . In $\text{Sc}_2(\text{MoO}_4)_3$ the mode at 80 cm^{-1} appears to be the lowest frequency mode. In analogy with the $\text{Zr}(\text{WO}_4)_2$ case, one can assign the 80 cm^{-1} mode to the librations of the MoO_4 tetrahedral ion.

As mentioned earlier, the structure of $\text{Sc}_2(\text{MoO}_4)_3$ consists of a corner-shared network of MoO_4 tetrahedra and ScO_6 octahedra. From the point of view of vibrational analysis one can treat either MoO_4 or ScO_6 as the polyatomic unit. The existence of such strongly bound molecular ions can be inferred from the presence of the corresponding internal modes. In the present Raman spectra of $\text{Sc}_2(\text{MoO}_4)_3$ and in those reported earlier [10], the internal modes associated with MoO_4 tetrahedra [13, 14] were identified while those of ScO_6 octahedra could not be identified. This suggests that MoO_4 is a much more strongly bound molecular ion-like unit compared to ScO_6 in this material. In this scenario one would expect only the lattice modes associated with Sc translation in the potential well of the surrounding oxygen atoms. The internal modes of MoO_4 tetrahedral ions are symmetric stretching ($\nu_1(A)$), antisymmetric stretching ($\nu_3(F)$), antisymmetric bending ($\nu_4(F)$) and symmetric bending ($\nu_2(E)$) modes. In a crystal, these modes exhibit splitting due to its lower site symmetry and Davydov

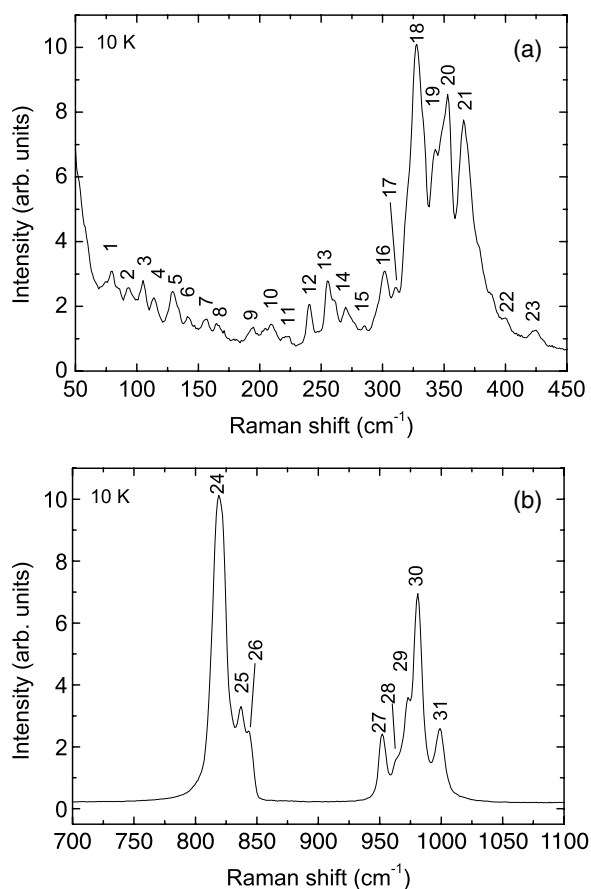


Figure 1. Raman spectra of monoclinic $\text{Sc}_2(\text{MoO}_4)_3$ at 10 K. (a) The low frequency region covering lattice modes and ν_2 and ν_4 bending modes of MoO_4 ion; (b) the high frequency region showing ν_1 and ν_3 molybdate stretching modes of MoO_4 ion.

(correlation) splitting. From the knowledge of the frequencies of the internal modes of MoO_4 tetrahedra in other molybdates such as $\text{Lu}(\text{MoO}_4)_2$ [13] and $\text{KAl}(\text{MoO}_4)_2$, $\text{RbAl}(\text{MoO}_4)_2$ and $\text{CsAl}(\text{MoO}_4)_2$ [14] one can identify regions corresponding to different internal modes. The modes in the frequency range 950–1000 cm^{-1} could be assigned to the symmetric stretching (ν_1) and those in the range 850–900 cm^{-1} to the antisymmetric stretching (ν_3) modes. These vibrations are associated with displacement of oxygen atoms against the central Mo atom. Several prominent peaks that appear between 300 and 450 cm^{-1} are identified as ν_2 and ν_4 bending modes of MoO_4 ions.

Figure 2 shows the Raman spectra of scandium molybdate at several temperatures in the heating cycle. Note that the spectra at 200 and 260 K exhibit distinct changes as compared to those of 14 and 150 K as a consequence of the structural transition from the monoclinic to the orthorhombic phase. In the high temperature orthorhombic phase only 24 modes could be identified unambiguously (table 2). The modes at 94, 142, 166, 210, 309, 401, 963 and 999 cm^{-1} disappear while a new mode at 388 cm^{-1} appears. Among the changes in the Raman intensities and discontinuities in mode frequencies, the most dramatic changes across the monoclinic–orthorhombic transition are (a) the appearance of a new mode at 388 cm^{-1} and (b) the disappearance of the 999 cm^{-1} mode. The intensity of the 388 cm^{-1} mode is found

Table 1. Mode frequencies and their temperature coefficients for monoclinic and orthorhombic $\text{Sc}_2(\text{MoO}_4)_3$. The numbers in parentheses represent the standard errors in the least significant digits.

Monoclinic phase (@10 K)		Orthorhombic phase (@170 K)		
Mode frequency (cm^{-1})	T -coefficient ($10^{-3} \text{ cm}^{-1} \text{ K}^{-1}$)	Mode frequency (cm^{-1})	T -coefficient ($10^{-3} \text{ cm}^{-1} \text{ K}^{-1}$)	
1	80	9(5)	83	-8(3)
2	94	—	—	—
3	105	8(4)	103	-24(11)
4	115	10(7)	112	-46(7)
5	129	5(7)	128	0 ^a
6	142	—	—	—
7	156	8(3)	158	-16(3)
8	166	20(9)	—	—
9	194	—	200	—
10	210	-8(6)	—	—
11	222	—	219	-17(5)
12	241	10(1)	248	-16(2)
13	255	13(3)	259	-12(2)
14	270	15(5)	270	—
15	285	—	288	-29(9)
16	302	16(2)	307	-22(7)
17	309	—	—	—
18	328	6(1)	328	0
19	342	—	342	—
20	353	9(6)	347	-17(3)
21	366	9(6)	361	-27(2)
22	401	—	388	-38(3)
23	424	5(6)	423	-46(9)
24	819	5(2)	821	-24(2)
25	837	5(2)	837	-20(3)
26	843	—	842	—
27	952	6(2)	955	-23(1)
28	963	—	—	—
29	974	—	973	—
30	981	7(3)	986	-26(2)
31	999	7(3)	—	—

^a The T -coefficient is set to zero when the standard error is greater than its value.

to increase gradually as a function of temperature while that of the 999 cm^{-1} mode decreases monotonically. Evolution of the intensities of these modes will be discussed later.

The dependences of mode frequencies on temperature are shown in figure 3. Note that distinct changes in the mode frequencies and changes of their slope take place as the sample undergoes a structural phase transition. Although the transition is reported to occur at 178 K from the x -ray diffraction studies [8], one can see in figure 3 that the modes of the orthorhombic phase are present even at 164 K. Since there are only minor changes in local structure/coordination associated with the monoclinic–orthorhombic transition as revealed by XRD studies [8], the corresponding change in phonon frequencies is also small. Several modes also become broad as temperature is increased, and closely positioned peaks merge. Broadening of modes arises mainly due to anharmonicity. The intensities of some modes decrease and they merge with the background. Only 20 out of 24 modes could be followed up to room temperature in the orthorhombic phase (table 1).

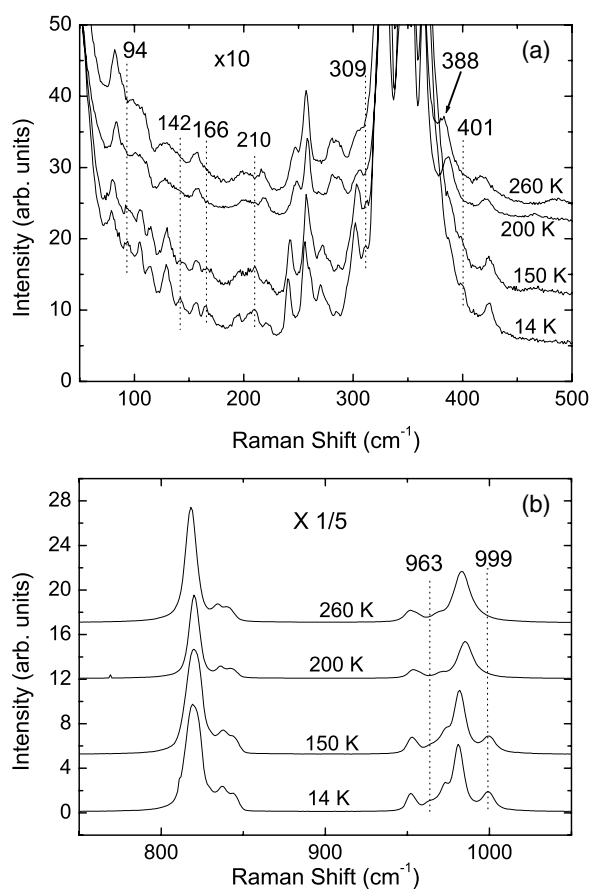


Figure 2. Raman spectra of $\text{Sc}_2(\text{MoO}_4)_3$ at different temperatures. During the heating cycle a phase transition from monoclinic to orthorhombic structure occurs at about 174 K. The modes that disappear in the orthorhombic phase are identified with vertical dotted lines. The new mode at 388 cm^{-1} is identified with an arrow mark.

Table 2. Mode Grüneisen parameters, ‘true anharmonic’ and ‘quasi-harmonic’ contributions to the total anharmonicity for the internal modes of the molybdate ion in the orthorhombic phase of $\text{Sc}_2(\text{MoO}_4)_3$.

Mode frequency $\omega \text{ (cm}^{-1}\text{)}$	γ_j	Total anharmonic (10^{-5} K^{-1})	Quasi-harmonic $\alpha\gamma_j \text{ (} 10^{-5} \text{ K}^{-1}\text{)}$	True anharmonic (10^{-5} K^{-1})
328	0.08	0	-0.05	-0.05
361	0.17	-4.9	-0.11	-5.01
821	-0.02	-2.9	+0.01	-2.89
837	0.01	-2.4	-0.01	-2.41
955	0.01	-2.4	-0.01	-2.41
986	0.05	-2.6	-0.03	-2.63

As mentioned earlier, the Raman spectra exhibit a gradual reduction in intensity and disappearance of the mode at 999 cm^{-1} , and the simultaneous appearance and growth in intensity of a new mode at 388 cm^{-1} in the heating cycle as one enters the orthorhombic phase at a temperature of $174 \pm 11 \text{ K}$. This is consistent with the phase transition temperature of 178 K

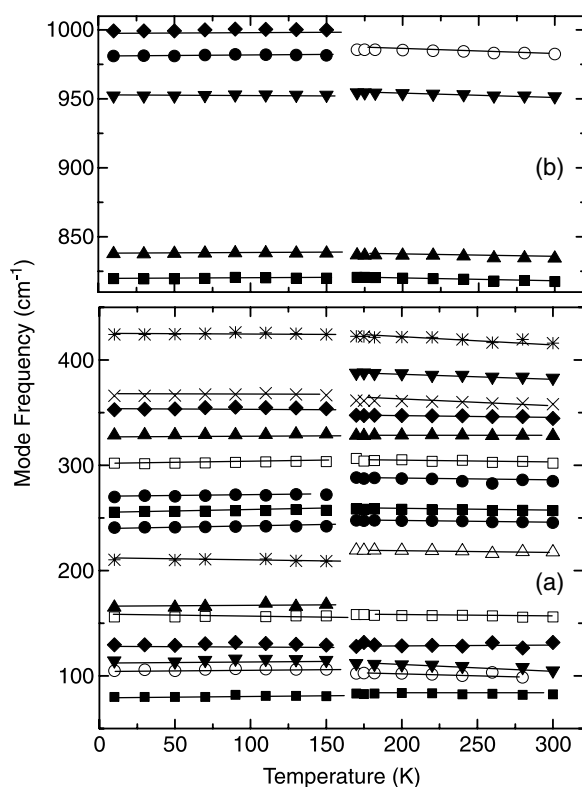


Figure 3. Mode frequencies of the various Raman modes as a function of temperature in monoclinic and orthorhombic phases. (a) Lattice, ν_2 and ν_4 modes, (b) ν_1 and ν_3 modes.

during heating cycle reported from XRD measurements [8]. Figure 4 shows the normalized intensities of 388 and 999 cm^{-1} modes as a function of temperature. In the cooling cycle, the reverse transition occurs at 142 ± 10 K, with a hysteresis of 32 K. It must be pointed out that the intensity data in figure 4 are equilibrium values and not an artifact of a slow/sluggish transition. The sample was soaked for 5–10 min after each temperature was reached. Also care was taken not to overshoot while changing temperature from one to the next. Temperature was controlled to within ± 0.1 K.

A structural phase transition that occurs upon cooling below room temperature could usually be expected to occur at ambient temperature and high pressure, since both pressure and low temperature reduce the volume and thus are often considered equivalent. From these considerations, one can expect the orthorhombic–monoclinic transition in $\text{Sc}_2(\text{MoO}_4)_3$ to occur at high pressure. Recently Paraguassu *et al* [15] have argued, on the basis of their high pressure Raman data, in favour of orthorhombic–monoclinic transition occurring at 0.29 GPa; however, they have not analysed their energy dispersive x-ray diffraction data to support their claim. On the other hand, recent angle dispersive x-ray diffraction results [10] do not show any evidence of this transition. In fact, the diffraction peaks of the orthorhombic phase are found to persist up to 11 GPa, above which the compound turns amorphous. Interestingly this compound also exhibits molybdate ion disorder at ambient and at high pressure [10]. This is inferred from the existence of a greater number of Raman peaks in the non-degenerate ν_1 internal mode region than predicted by group theory. The existence of orientational disorder of tetrahedral molecular ions such as SO_4^{2-} in double sulfates has been shown to prevent structural

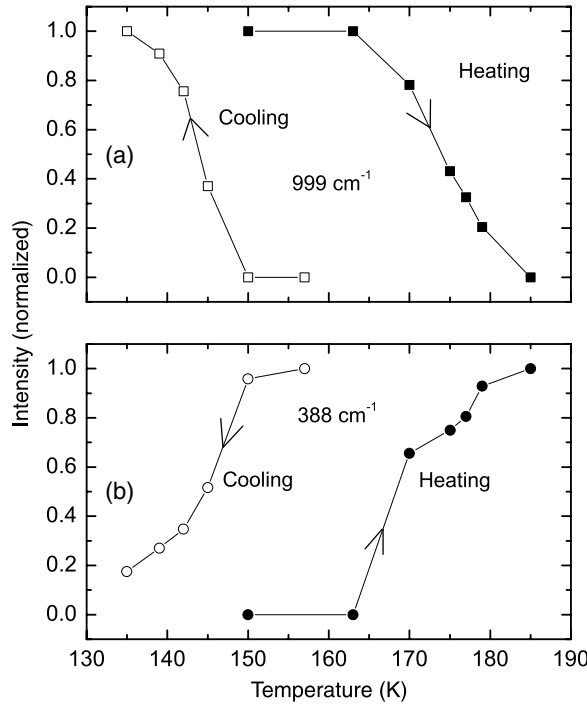


Figure 4. Intensities of (a) 999 and (b) 388 cm^{-1} modes as a function of temperature during heating and cooling cycles.

phase transitions and eventually lead to amorphization of the material [16, 17]. In view of this it is likely that in the case of $\text{Sc}_2(\text{MoO}_4)_3$ the rapid evolution of molybdate ion disorder at high pressure also preempts the orthorhombic–monoclinic transition and results in amorphization.

In a material with positive thermal expansion, the vibrational frequencies normally decrease as temperature is increased, and vice versa [18–20]. This is because the lattice expansion increases the interatomic distances, thereby reducing the force constants of the various bonds as temperature is increased. In contrast to this, the temperature coefficients of phonon frequencies in the monoclinic phase exhibit opposite behaviour. The low temperature monoclinic phase exhibits positive thermal expansion, and thus the temperature coefficients would be expected to be negative. However, most of the mode frequencies exhibit positive temperature coefficients. On the other hand, for the high temperature orthorhombic phase one finds negative slopes for many of the modes. In order to understand these behaviours, we obtain the anharmonicities of the different phonon modes.

The temperature dependence of the phonon mode frequency at constant pressure can be resolved into two components, one that arises from the change in volume (called the ‘quasi-harmonic’ or ‘implicit’ contribution) and another, purely anharmonic contribution (at constant volume) due to the changes in vibrational amplitudes at fixed equilibrium positions (called the ‘explicit’ contribution) [4]. Thus the total normalized temperature dependence can be written as

$$\frac{1}{\omega_j} \left. \frac{d\omega_j}{dT} \right|_P = \frac{1}{\omega_j} \left. \frac{\partial \omega_j}{\partial T} \right|_V - \gamma_j \alpha \quad (1)$$

where $\gamma_j = -\partial \ln \omega_j / \partial \ln V = (B/\omega_j)(\partial \omega_j / \partial P)$ (where B is the bulk modulus) are mode Grüneisen parameters and $\alpha = V^{-1}(\partial V / \partial T)$ is the thermal expansion coefficient. Here the

first term on the right-hand side is the ‘true anharmonic’ contribution and the second is the ‘quasi-harmonic’ term.

The mode Grüneisen parameters for several of the modes in the orthorhombic phase could be obtained from the reported pressure dependence of the phonon frequency data [10]. For this a value of 6 GPa was used for the bulk modulus [11]. Below 200 cm^{-1} the modes were too weak in intensity (figure 2) to follow as a function of pressure. The values of the ‘total anharmonicity’ of the modes for which the pressure dependence has been reported are presented in table 2 along with their ‘quasi-harmonic’ components and the estimated ‘true anharmonicities’. However, no high pressure data are available for the monoclinic phase. Note from table 2 that the ‘quasi-harmonic’ contribution for all modes studied is small; thus the ‘true anharmonicities’ are nearly the same as the total anharmonicities. The values of the ‘true anharmonicity’ for all modes except the 328 cm^{-1} mode are negative and large. The 342 and 353 cm^{-1} modes are the ν_4 antisymmetric bending modes of the molybdate ion, and other higher frequency modes are symmetric and antisymmetric stretching modes. In particular, the 353 cm^{-1} mode seems to have a rather high anharmonicity. Nevertheless, these values are an order of magnitude lower than those of some of the low frequency and other highly anharmonic modes of $\text{Zr}(\text{WO}_4)_2$ [4], reflecting the low value of the thermal expansion of orthorhombic $\text{Sc}_2(\text{MoO}_4)_3$ ($\alpha = -6.3 \times 10^{-6}\text{ K}^{-1}$). Stretching modes have similar magnitude of anharmonicity to those of $\text{Zr}(\text{WO}_4)_2$. Measurements of Grüneisen parameters of low frequency modes would be useful in understanding the NTE behaviour of the orthorhombic phase. As the magnitude of the thermal expansion ($\alpha \sim +2.19 \times 10^{-5}\text{ K}^{-1}$) in the monoclinic phase is of the same order as that of the orthorhombic phase it is likely that the ‘quasi-harmonic’ contribution to the temperature coefficient of the phonon frequencies in this phase is also a small fraction of the total anharmonic temperature coefficient. Hence it may be reasonable to treat the ‘true anharmonicity’ as being nearly the same as the total anharmonicity in the monoclinic phase also. Thus these results suggest that most of the phonons in the monoclinic phase have positive anharmonicity; i.e., the temperature coefficient of the phonon frequencies is positive. This can occur if the potential wells for the atomic vibrations (at constant volume) become steeper at higher temperatures (a positive quartic term in the potential), making the corresponding force constants stiffer. On the other hand, the orthorhombic phase, which is less densely packed than the monoclinic phase, exhibits negative anharmonicity implying that phonons become soft at higher temperature. This is a normal behaviour found in most materials. The opposite natures of the anharmonicities in the two phases essentially arises due to the extent of free space (packing) between corner-linked polyhedral units in the network structure.

4. Summary and conclusions

The orthorhombic to monoclinic phase transition in $\text{Sc}_2(\text{MoO}_4)_3$ was investigated using Raman spectroscopy. Monoclinic and orthorhombic phases are found to coexist between 163 and 185 K in the heating cycle. There is a large hysteresis of 32 K in this structural phase transition. The reverse transition in the cooling cycle takes place over a ~ 20 K range around 142 K. Temperature coefficients of phonon frequencies are negative in the orthorhombic phase and positive in the monoclinic phase, suggesting strong anharmonicities of phonons. Analysis using reported mode Grüneisen parameters indicates that the bending modes of MoO_4 ions are the most anharmonic among the modes studied.

Acknowledgments

We thank Dr T A Mary for providing the samples for this study. We thank Dr B Viswanathan for his interest in the work, Dr S L Mannan for support and Dr Baldev Raj for encouragement.

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