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Raman spectroscopy of $MnWO_4$

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The polarized Raman spectra of $MnWO_4$ single crystals were studied between 5 and 300 K. All $8A_g + 10B_g$ Raman active modes were identified and assigned to definite atomic motions in close comparison with the frequencies and eigenvectors predicted by shell model calculations. No detectable phonon anomalies were observed near the three successive magnetic and ferroelectric transitions at 13.5, 12.5, and 6.8 K.

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I. INTRODUCTION

$MnWO_4$ belongs to the group of metal tungstates with wolframite $P2/c$ structure (space group #13, Z=2) shown in Fig. 1. In the last few years it attracts increased attention as a multiferroic material with intriguing magnetic phase diagram below 15 K.[1–6] At low temperatures there are three antiferromagnetically ordered states, AF3, AF2, and AF1 with transition temperatures $T_N \approx 13.5$ K, $T_2 \approx 12.5$ K, and $T_1 \approx 7$ K. In the AF1 ($T < T_1$) and AF3 ($T_2 < T_N$) the magnetic moments are aligned collinearly in the *ac* plane with incommensurate and commensurate propagation, respectively. The magnetic moments in the AF2 phase ($T_1 < T < T_2$) have a component in the *b* direction that gives rise to cycloidal magnetic order. Simultaneously ferroelectric polarization appears in the AF2 phase. The ferroelectricity associated with AF2 ordering suggests noticeable spin-lattice coupling thus attracting interest to the phonons in $MnWO_4$ and possible phonon anomalies near the magnetic transitions. The lattice dynamics of some isostructural compounds, such as $CdWO_4$ and $ZnWO_4$ has been studied in detail, both experimentally and theoretically.[7–9] The reports on the phonons in $MnWO_4$, however, are restricted mainly to the unpolarized Raman spectra of wolframite [$(Mn/Fe)WO_4$) and hübnerite ($MnWO_4$) minerals at room temperature.[10–13] In this work we present the polarized Raman spectra of $MnWO_4$ single crystals obtained in several exact scattering configurations. All $8A_g + 10B_g$ Raman modes are clearly identified and assigned to particular atomic vibrations by comparison to the calculations of lattice dynamics. The variation in the Raman spectra with lowering temperature down to 5 K, however, exhibits no detectable anomalies that could be related to the magnetic and/or ferroelectric transitions.

II. SAMPLES AND METHODS

Single crystals of $MnWO_4$ were grown by high-temperature solution growth method. As a first step polycrystalline $MnWO_4$ was synthesized by solid state reaction of stoichiometric amounts of MnO_2 and WO_3 annealed for 48 h in air at 1050 °C. After grinding the $MnWO_4$ powder was mixed in a 1:20 ratio with $0.5Na_2WO_4 + 0.5WO_3$ flux and heated for 12 h at 1150 °C in a platinum crucible. The single crystals were obtained by slow cooling at the rate of 0.5 °C/h in the temperature range 1100–860 °C. At 860 °C the crystals were separated from the residual flux by decanting. The dark crystals with semimetallic luster removed from the bottom of the crucible were of rectangular shape and of typical size $5 \times 3 \times 2$ mm^3.

The ac magnetic susceptibility measured at 10 Oe, 10 Hz (Fig. 2) revealed the known successive antiferromagnetic transitions at $T_N = 13.5$ K to the AF3 structure (commensurate collinear), AF2 structure (commensurate spiral, which is also ferroelectric) at $T_2 = 12.5$ K, and finally to the low temperature AF1 structure (incommensurate collinear) below $T_1 = 6.8$ K.

The Raman spectra were measured under microscope in backward scattering configuration from the *ab*, *ac*, and *bc* as-grown surfaces of $MnWO_4$ single crystals using a T64000 (Horiba-Jobin Yvon) Raman spectrometer. Except for slight differences in the relative amplitude of the peaks, the spectra obtained with 633 nm (He-Ne) and 515, 488, and 458 nm (Ar^+) excitation were practically identical. In the low temperature measurements the sample was cooled in a Microstat^{He} (Oxford instruments) optical cryostat where the temperature could be varied between 4 and 300 K. In these

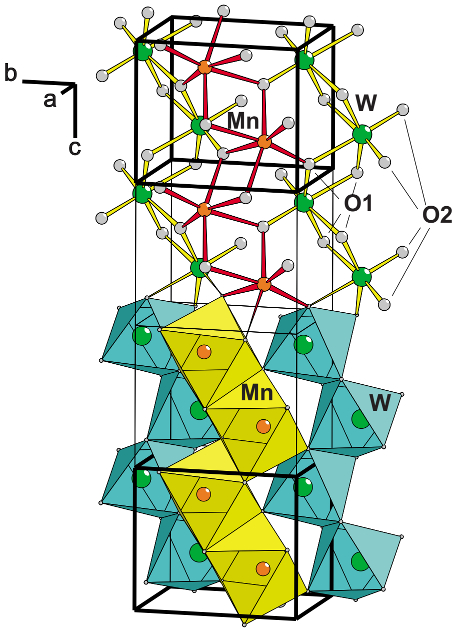

FIG. 1. (Color online) Unit cell of $MnWO_4$ (space group $P2/c$, Z=2).

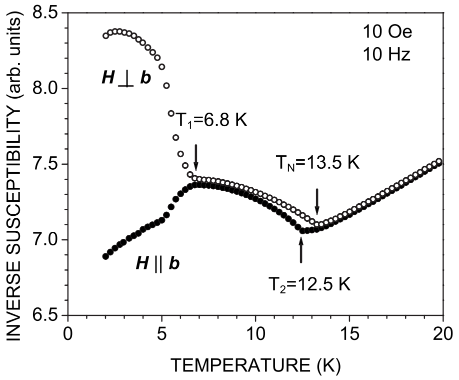

FIG. 2. Inverse AC susceptibility of $MnWO_4$ near the successive magnetic transitions.

measurements the incident laser power focused down to a spot of 2 μm diameter was kept below 0.1 mW to avoid local heating. Lattice dynamical calculations were performed within a shell model using the General Utility Lattice Program (Ref. 14) using the crystallographic data reported in Ref. 15.

III. RESULTS AND DISCUSSION

Figure 3 shows the Raman spectra of $MnWO_4$ as measured with several exact scattering configurations at 300 K. The A_g and B_g modes are readily distinguished as the former are allowed with XX, YY, ZZ, and XY but forbidden with XZ and YZ polarization and vice versa. The first and second letters in these notations correspond to the polarization direction of the incident and scattered light, respectively. All eight A_g and ten B_g modes expected from symmetry considerations

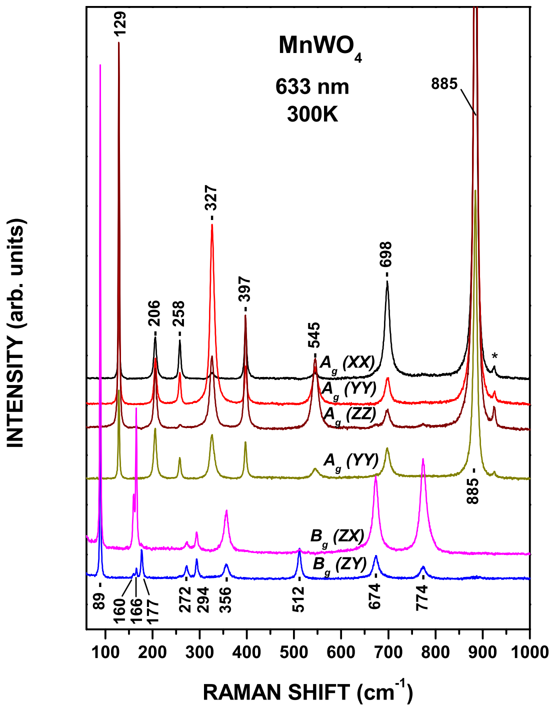

FIG. 3. (Color online) Polarized Raman spectra of $MnWO_4$ obtained at room temperature with 633 nm excitation line. The asterisk "*" denotes a peak from impurity phase.

TABLE I. Raman phonon frequencies (in cm^{-1}) of $MnWO_4$, $ZnWO_4$, and $CdWO_4$.

Mode	$MnWO_4$ LDC 0 K	$MnWO_4$ exp 5 K/300 K	$ZnWO_4$ Ref. 9 300 K	$CdWO_4$ Ref. 8 300 K	Main atomic motions
$A_g(1)$	125	131/129	123	100	Mn(y)W(y)
$A_g(2)$	195	209/206	196	177	W(y)Mn(y)
$A_g(3)$	280	259/258	276	229	O2(xyz)W(y)Mn(y)
$A_g(4)$	330	329/327	342	306	O2(yz)O1(xyz)Mn(y)
$A_g(5)$	453	398/397	407	388	O2(xy)O1(xz)W(y)
$A_g(6)$	551	549/545	546	546	O1(yz)O2(xyz)Mn(y)W(y)
$A_g(7)$	639	698/698	709	707	O1(xz)W(y)
$A_g(8)$	830	885/885	907	897	O2(xyz)W(y)
$B_g(1)$	123	91/89	92	78	W(xz)Mn(x)
$B_g(2)$	150	161/160	146	118	Mn(z)W(z)
$B_g(3)$	173	167/166	164	134	W(xz)O1(xyz)
$B_g(4)$	248	178/177	190	148	Mn(xz),W(xz)
$B_g(5)$	309	275/272	267	249	Mn(xz)W(xz)O2(yz)
$B_g(6)$	334	296/294	313	269	Mn(z)W(xz)O1(xz)O2(xy)
$B_g(7)$	406	360/356	354	352	O2(xyz)W(z)Mn(z)
$B_g(8)$	482	514/512	515	514	O1(xyz)O2(x)
$B_g(9)$	674	674/674	678	688	O1(xz)
$B_g(10)$	758	776/774	786	771	O2(xyz)W(xz)

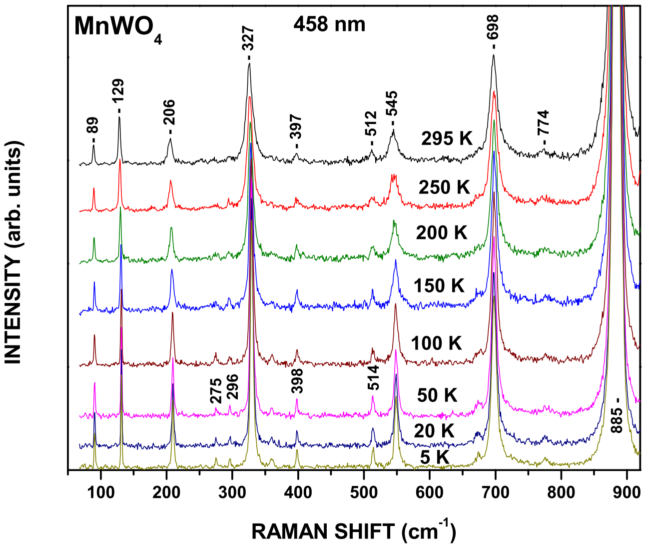

FIG. 4. (Color online) Temperature-dependent Raman spectra of $MnWO_4$.

are clearly pronounced. The experimental values of the phonon frequencies are compared to those predicted by the shell model lattice dynamic calculations (LDC), proven to adequately describe vibrational spectrum of metal oxides,[16] and to the corresponding modes of isostructural $ZnWO_4$ and $CdWO_4$ in Table I. The main atomic motions as determined by LDC are also given. As expected, the high frequency modes governed by stretching O-W vibrations are very close for all three compounds whereas the modes involving motions of divalent cations decrease in frequency following the mass increase sequence Mn-Zn-Cd.

Figure 4 shows the spectra of $MnWO_4$ at various temperatures obtained in a mixed scattering configuration allowing observation of both A_g and B_g modes. The decrease in temperature down to ≈50 K results in standard sharpening and weak shift of the Raman lines toward higher wave numbers. The relative change with temperature $\omega(T)/\omega(5\text{ K})$ of the frequency of the most pronounced modes is illustrated in Fig. 5. The total hardening between 300 and 5 K of the high frequency $A_g(7)$ and $A_g(8)$ modes is extremely small (≃0.1%) whereas the low frequency modes exhibit much larger shift of up to 2.5%.

In a search for possible effect of magnetic and ferroelectric transitions we studied more carefully the phonon parameters between 5 and 20 K. Within the experimental accuracy of 0.1–0.2 cm^{-1} both the positions and the widths of all Raman lines were practically constant in this temperature range. This finding is somewhat unexpected as ferroelectricity associated with magnetic ordering presupposes relatively strong spin-lattice interaction and magnetic-order-induced structural changes. The lack of detectable anomaly in the phonon frequency, however, is consistent with recently reported[5] very weak changes of lattice parameters $\Delta a/a \approx -3\times10^{-5}$, $\Delta b/b \approx -1\times10^{-5}$, and $\Delta c/c \approx 1\times10^{-5}$ associated with the transition(s).

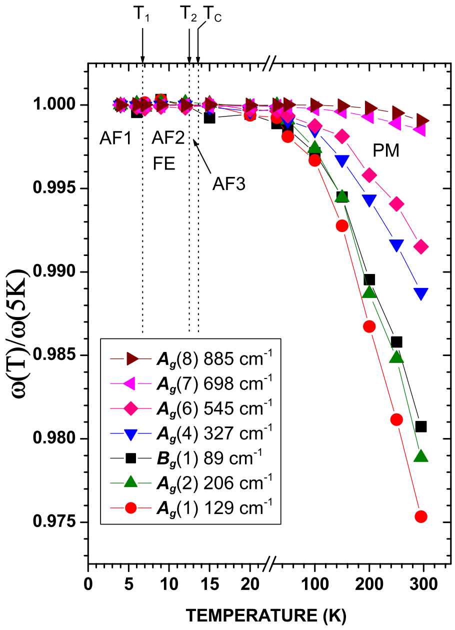

FIG. 5. (Color online) Relative change with temperature of $\omega(T)/\omega(5\text{ K})$ of the frequency of the most pronounced Raman modes of $MnWO_4$.

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