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LETTER TO THE EDITOR

Spin–phonon coupling in rod-shaped half-metallic CrO_2 ultrafine particles: a magnetic Raman scattering study

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Abstract
Half-metallic CrO_2 powder compact with rod-shaped nanoparticles was studied by micro-Raman scattering in the presence of an external magnetic field at room temperature (300 K). In the low-field region ($H \leqslant 250$ mT), the frequency and intensity of the E_g mode, an internal phonon mode of CrO_2, increase dramatically with increase in the magnetic field, while the corresponding linewidth decreases. The above parameters become constant when the CrO_2 powder enters the saturation state at higher magnetic field. The pronounced anomalies of the Raman phonon parameters under a low magnetic field are attributed to the spin–phonon coupling enhanced by the magnetic ordering, which is induced by the external magnetic field.

Chromium oxide, CrO_2, has long been of importance in magnetic recording and shows unique magnetic properties. Schwarz [1] was the first to predict that CrO_2 is a half-metallic material, using self-consistent band structure calculation. Following his work, several experiments have been carried out that suggest the existence of half-metallicity in CrO_2. Kamper *et al* [2] used photoemission spectroscopy and Wiesendanger *et al* [3] reported vacuum tunnelling measurement, while superconducting point-contact experiments were carried out by Soulen *et al* [4]. With this half-metallic property of nearly 100% spin polarization at the Fermi level [2–4], ferromagnetic CrO_2 was expected to be an ideal material for use as electrodes in spin-dependent tunnelling devices [5] and to show an extremely large tunnelling magnetoresistance (TMR). Comparing with single-crystal CrO_2, showing little magnetoresistance (MR) below $T_c \sim 397$ K [6], polycrystalline thin film and cold-pressed powder CrO_2 exhibit high MR values [7, 8]. By introducing an interface barrier of Cr_2O_3, a dramatically enhanced MR effect

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$\sim$50% was found in cold-pressed powder consisting of CrO_2 and Cr_2O_3 nanoparticles [9]. Huge MR ($\sim$41%) was also reported in aligned CrO_2 nanorods, where magnetic anisotropy was observed [10]. Our laser annealing study of CrO_2 powder demonstrated that the MR could be easily controlled by adjusting the ratio of CrO_2 and Cr_2O_3 decomposed at the surface of CrO_2 nanorods in a selected micro-region [11]. Thus, cold-pressed CrO_2 powder, especially CrO_2 nanorods with huge surfaces and interfaces, is attractive in research and potentially in applications as a promising precursor for developing high-density and high-efficiency TMR devices.

Recently, Raman scattering has shown its significant advantages in investigating giant-magnetoresistance (GMR) [12], colossal-magnetoresistance (CMR) [13], and tunnelling MR materials [14]. In particular, Raman scattering studies on the strong spin–phonon coupling, so-called polarons [15, 16], have contributed significantly to the understanding of electronic transport properties in such MR materials. However, few Raman scattering studies have been carried out to investigate half-metallic CrO_2 [17, 18]. CrO_2 is a metastable phase [19], and it can be decomposed into Cr_2O_3, which shows strong Raman peaks compared with CrO_2, by a laser beam at a relatively low power [11]. In this letter, we present the first micro-Raman scattering study on cold-pressed half-metallic CrO_2 powder compact in the presence of an external magnetic field. More importantly, in previous Raman scattering studies [20, 21], the ambient temperature was changed to trigger or enhance spin–phonon coupling. This variation of temperature strongly affects the phonon modes by introducing an anharmonic effect and makes such phonon behaviour more complex [20]. In this work, the ambient temperature was fixed at room temperature (300 K).

Our CrO_2 samples were prepared from commercial powders (DuPont, 99.5%) used for magnetic recording. After being cold pressed into discs, the original CrO_2 powders were systematically analysed. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) were employed to characterize the phase purity and morphology of the CrO_2 powder respectively. The magnetic properties, such as the coercivity and saturation magnetization of the original CrO_2 powder, were measured using a vibrating sample magnetometer (VSM, 41719.7 Oxford Instruments). All micro-Raman spectra were measured in the backscattering geometry using an ISA T64000 Raman spectrometer with an Olympus microscope attachment and equipped with a liquid-nitrogen-cooled CCD detector. The 514 nm line of an argon-ion laser was used as the excitation source. In order to avoid sample degradation, i.e. the decomposition of CrO_2 into Cr_2O_3, the power of the focused laser beam on the sample surface was limited to 2 mW. The external magnetic field was varied from zero field (ZF) to 500 mT with the ambient temperature fixed at 300 K.

Figure 1(a) shows the XRD pattern of the original CrO_2 powder. Only well established diffraction peaks of the polycrystalline phase CrO_2 were present and no peaks belonging to the Cr_2O_3 phase were observed [22]. This indicates that the original CrO_2 sample is of high purity and contains no measurable Cr_2O_3. Figure 1(b) shows the SEM image of the CrO_2 powder, showing the elongated rod-shaped CrO_2 particles with an aspect ratio of about 8:1 and average length of about 300 nm, oriented randomly. As shown in figure 1(c), the CrO_2 powder is ferromagnetic at room temperature (300 K). The coercivity and saturation magnetization are 86 mT and 87 emu g^{-1} respectively.

Figure 2 shows the room temperature Raman spectra of half-metallic CrO_2 powder at ZF and at a low magnetic field up to 500 mT. It is seen that the room temperature ZF Raman scattering spectrum is mainly characterized by two peaks at 455.4 and 573.9 cm^{-1}, corresponding to the vibrational modes of E_g and A_{1g} symmetries [17]. These two Raman-active modes are internal phonon modes, involving only vibrations of the oxygen atoms which form the sublattice CrO_6 octahedron [17]. Upon applying a magnetic field, the Raman phonon (E_g mode) parameters: frequency, intensity, and linewidth, show pronounced anomalies.

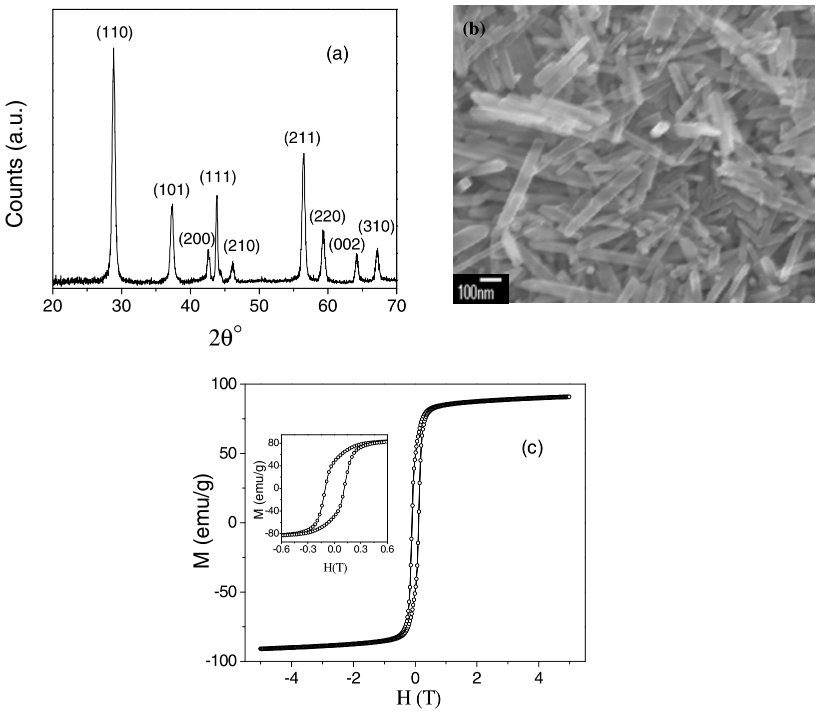

Figure 1. (a) XRD patterns, (b) the SEM image, and (c) the hysteresis loop of half-metallic CrO_2 powder at room temperature (300 K). The inset shows detail at low field.

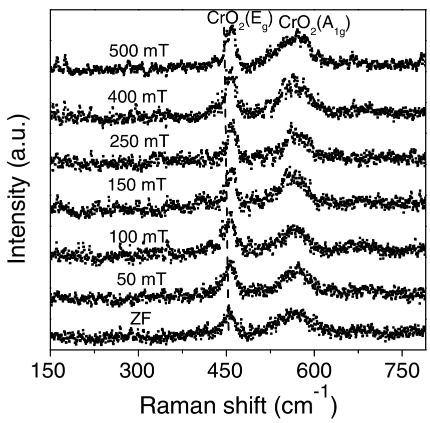

Figure 2. The magnetic field dependence of the room temperature Raman spectra of half-metallic CrO_2 powder.

In order to study the variation of the E_g mode in the presence of an external magnetic field shown in figure 3(a), a least-squares fit with Lorentzian line-shape was used to fit the Raman peak of the E_g mode. Figure 3(b) shows the fitted full width at half-maximum (FWHM), peak intensity, and position of the E_g mode as a function of the applied magnetic field. In the presence of a relatively low magnetic field ($H < 250$ mT), the frequency and intensity of the E_g mode show an obviously monotonic increase with increase in strength of the magnetic field

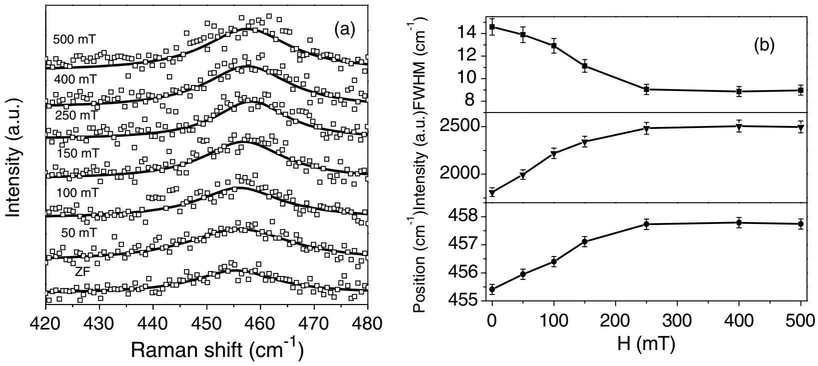

Figure 3. (a) Detailed Raman spectra of the E_g mode under a magnetic field. The open squares show experimental data and the lines show data fitted using Lorentzian line-shapes. (b) The parameters of the E_g mode as a function of magnetic field.

while the linewidth decreases monotonically. When the applied magnetic field was within the range of 250–500 mT, where the CrO_2 powder entered the saturation state (see figure 1(c)), no pronounced change of the Raman phonon parameters was observed.

Three possible physical mechanisms may lead to measurable anomalies of Raman phonon parameters or even activation of a new Raman mode in a magnetic ordering system. The first mechanism is a structural transition. A typical material exhibiting this mechanism is cupric oxide CuO [23]. Due to the folded zone from the Z′ point of the Brillouin-zone boundary, this material exhibits new Raman-active lines upon entering the magnetically ordered state. The second mechanism is the anharmonic effect which is involved in all temperature-induced magnetic ordering systems. The last one is spin–phonon coupling. The first two mechanisms are not active in the present case, since the ambient temperature is fixed at 300 K, and, to our knowledge, no data on low-magnetic-field ($H \leqslant 500$ mT) variation of the structure are available for cold-pressed powder compact CrO_2. Thus, it is reasonable to attribute the anomalies of the Raman mode observed in this work to the spin–phonon coupling. Similar anomalies of the Raman phonon in half-metallic CrO_2 were reported by Iliev *et al* [17], where anomalous broadening of phonon lines, in addition to the broadening induced by the normal phonon–phonon scattering (anharmonic decay), was observed when the temperature was increased to T_c. This additional broadening was attributed to collective spin fluctuations near T_c, which results in spin disorder scattering. In the present work, the spin ordering was controlled by an external magnetic field and the degree of spin ordering was measured using Raman spectroscopy via spin–phonon interaction. A higher external magnetic field results in a more ordered spin state that in turn gives rise to sharper Raman bands. Hence the Raman linewidths will decrease with increasing magnetic field. As the temperature was fixed at room temperature in our study, our results are free from the anharmonic broadening effect, making spectral interpretation simpler and more definitive. Our study complements that of [17]. The temperature was slightly above T_c in [17] and no definite conclusion was drawn about the effect of spin on the phonon frequencies. However, in their study of another ‘bad’ metal, $SrRuO_3$ [24], the spin–phonon coupling was investigated in detail. According to the above studies, the observed anomalies of the E_g mode in this work could be explained as follows. Upon applying an external magnetic field, the magnetic ordering of CrO_2 was enhanced due to the higher degree of spin alignment. This magnetic ordering subsequently increased the interaction among the neighbouring Cr ions. Due to the high sensitivity to the interaction among Cr ions, the Cr–O bond length and bond angle in the CrO_6 octahedron were also changed, resulting in anomalous change in the internal Raman mode, the E_g mode in this work. The narrowing of the linewidth and increase in peak intensity are direct evidence of increased ordering of the CrO_6 octahedron. In our previous magnetic Raman scattering study on spinel $CoFe_2O_4$ [25], the magnetism–lattice interaction was demonstrated by the red-shift of the Raman modes. Future work, i.e. polarized Raman scattering study of aligned or isolated CrO_2 nanorods, is believed to be very important for revealing the mechanism of the MR effect and magnetic anisotropy.

In conclusion, an inelastic light-scattering study of rod-shaped CrO_2 ultrafine powder was performed in a low magnetic field. The E_g mode of the CrO_2 powder showed pronounced anomalies upon applying an external magnetic field, and these anomalies of the Raman phonon parameters were attributed to the spin–phonon coupling induced by magnetic-field-enhanced magnetic ordering. The results of this work demonstrate that Raman scattering, especially magnetic Raman scattering, could be an effective tool for the understanding of the practically important TMR material CrO_2.

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