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## LETTER TO THE EDITOR

## Spin–phonon coupling in rod-shaped half-metallic CrO<sub>2</sub> ultrafine particles: a magnetic Raman scattering study

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### Abstract

Half-metallic CrO<sub>2</sub> 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 ( $H \leq 250$  mT), the frequency and intensity of the E<sub>g</sub> mode, an internal phonon mode of CrO<sub>2</sub>, increase dramatically with increase in the magnetic field, while the corresponding linewidth decreases. The above parameters become constant when the CrO<sub>2</sub> 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<sub>2</sub>, has long been of importance in magnetic recording and shows unique magnetic properties. Schwarz [1] was the first to predict that CrO<sub>2</sub> 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<sub>2</sub>. 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<sub>2</sub> 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<sub>2</sub>, showing little magnetoresistance (MR) below  $T_c \sim 397$  K [6], polycrystalline thin film and cold-pressed powder CrO<sub>2</sub> exhibit high MR values [7, 8]. By introducing an interface barrier of Cr<sub>2</sub>O<sub>3</sub>, a dramatically enhanced MR effect

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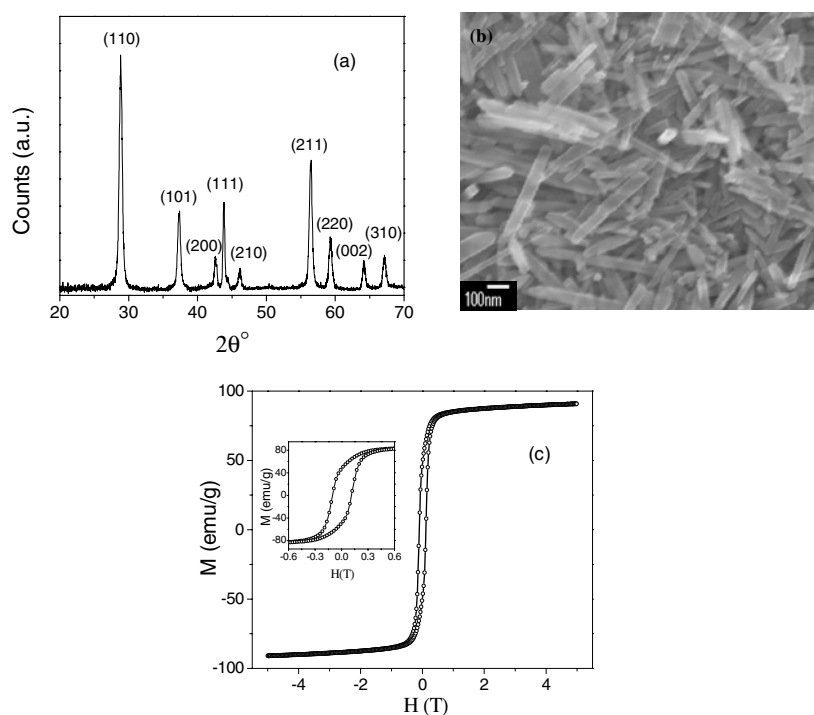
~50% was found in cold-pressed powder consisting of CrO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> nanoparticles [9]. Huge MR (~41%) was also reported in aligned CrO<sub>2</sub> nanorods, where magnetic anisotropy was observed [10]. Our laser annealing study of CrO<sub>2</sub> powder demonstrated that the MR could be easily controlled by adjusting the ratio of CrO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> decomposed at the surface of CrO<sub>2</sub> nanorods in a selected micro-region [11]. Thus, cold-pressed CrO<sub>2</sub> powder, especially CrO<sub>2</sub> 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<sub>2</sub> [17, 18]. CrO<sub>2</sub> is a metastable phase [19], and it can be decomposed into Cr<sub>2</sub>O<sub>3</sub>, which shows strong Raman peaks compared with CrO<sub>2</sub>, 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<sub>2</sub> 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).

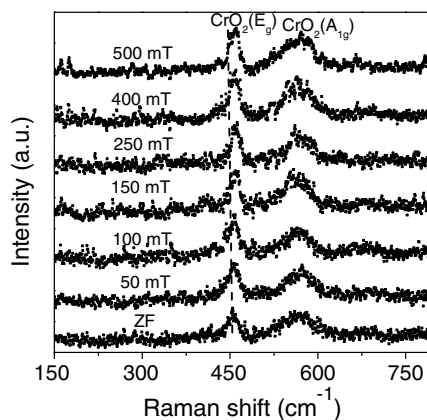
Our CrO<sub>2</sub> samples were prepared from commercial powders (DuPont, 99.5%) used for magnetic recording. After being cold pressed into discs, the original CrO<sub>2</sub> powders were systematically analysed. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) were employed to characterize the phase purity and morphology of the CrO<sub>2</sub> powder respectively. The magnetic properties, such as the coercivity and saturation magnetization of the original CrO<sub>2</sub> 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<sub>2</sub> into Cr<sub>2</sub>O<sub>3</sub>, 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<sub>2</sub> powder. Only well established diffraction peaks of the polycrystalline phase CrO<sub>2</sub> were present and no peaks belonging to the Cr<sub>2</sub>O<sub>3</sub> phase were observed [22]. This indicates that the original CrO<sub>2</sub> sample is of high purity and contains no measurable Cr<sub>2</sub>O<sub>3</sub>. Figure 1(b) shows the SEM image of the CrO<sub>2</sub> powder, showing the elongated rod-shaped CrO<sub>2</sub> 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<sub>2</sub> powder is ferromagnetic at room temperature (300 K). The coercivity and saturation magnetization are 86 mT and 87 emu g<sup>-1</sup> respectively.

Figure 2 shows the room temperature Raman spectra of half-metallic CrO<sub>2</sub> 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<sup>-1</sup>, corresponding to the vibrational modes of E<sub>g</sub> and A<sub>1g</sub> symmetries [17]. These two Raman-active modes are internal phonon modes, involving only vibrations of the oxygen atoms which form the sublattice CrO<sub>6</sub> octahedron [17]. Upon applying a magnetic field, the Raman phonon (E<sub>g</sub> mode) parameters: frequency, intensity, and linewidth, show pronounced anomalies.

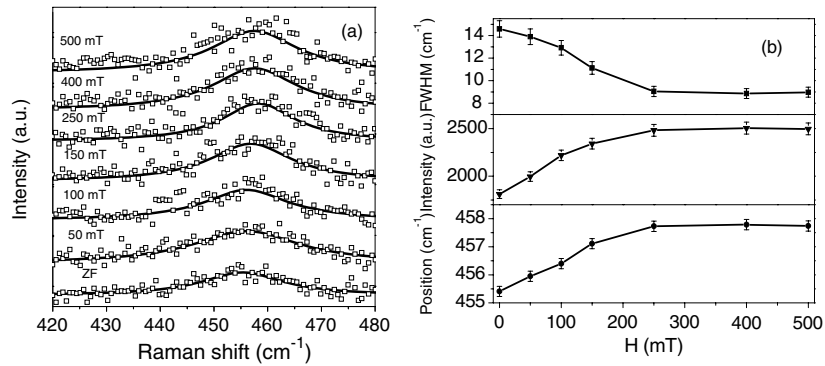


**Figure 1.** (a) XRD patterns, (b) the SEM image, and (c) the hysteresis loop of half-metallic  $\text{CrO}_2$  powder at room temperature (300 K). The inset shows detail at low field.



**Figure 2.** The magnetic field dependence of the room temperature Raman spectra of half-metallic  $\text{CrO}_2$  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  $\text{CrO}_2$  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  $\text{CuO}$  [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 ( $H \leq 500$  mT) variation of the structure are available for cold-pressed powder compact  $\text{CrO}_2$ . 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  $\text{CrO}_2$  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,  $\text{SrRuO}_3$  [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  $\text{CrO}_2$  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<sub>6</sub> octahedron were also changed, resulting in anomalous change in the internal Raman mode, the E<sub>g</sub> mode in this work. The narrowing of the linewidth and increase in peak intensity are direct evidence of increased ordering of the CrO<sub>6</sub> octahedron. In our previous magnetic Raman scattering study on spinel CoFe<sub>2</sub>O<sub>4</sub> [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<sub>2</sub> 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<sub>2</sub> ultrafine powder was performed in a low magnetic field. The E<sub>g</sub> mode of the CrO<sub>2</sub> 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<sub>2</sub>.

## References

- [1] Schwarz K 1986 *J. Phys. F: Met. Phys.* **16** L211
- [2] Kamper K P, Schmitt W, Güntherodt G, Gambino R J and Ruf R 1987 *Phys. Rev. Lett.* **59** 2788
- [3] Wiesendanger R, Güntherodt H J, Güntherodt G, Gambino R J and Ruf R 1990 *Phys. Rev. Lett.* **65** 247
- [4] Soulen R J, Byers J M, Osofsky M S, Nadgorny B, Ambrose T, Cheng S F, Broussard P R, Tanaka C T, Nowak J, Moodera J S, Berry A and Coey J M D 1998 *Science* **282** 85
- [5] Moodera J S, Kinder L R, Wong T M and Meservey R 1995 *Phys. Rev. Lett.* **74** 3273
- [6] Kouvel J S and Rodbell D S 1967 *J. Appl. Phys.* **38** 979
- [7] Hwang H Y and Cheong S-W 1997 *Science* **278** 1607
- [8] Manoharan S S, Elefant D, Reiss G and Goodenough J B 1998 *Appl. Phys. Lett.* **72** 984
- [9] Coey J M D, Berkowits A E, Balcells L, Putris F F and Barry A 1998 *Phys. Rev. Lett.* **80** 3815
- [10] Dai J B and Tang J K 2001 *Phys. Rev. B* **63** 544341
- [11] Yu T, Shen Z X, He J, Sun W X, Tang S H and Lin J Y 2003 *J. Appl. Phys.* **93** 3952
- [12] Li J M, Huan A C H, Wang L, Du Y W and Feng D 2000 *Phys. Rev. B* **61** 6876
- [13] Dediu V, Ferdeghini C, Maticotta F C, Nozar P and Ruani G 2000 *Phys. Rev. Lett.* **84** 4489
- [14] Yuan C L, Zhu Y, Ong P P and Yu T 2003 submitted
- [15] Deleon J M, Batistic I, Bishop A R, Conradson S D and Trugman S A 1992 *Phys. Rev. Lett.* **68** 3236
- [16] Millis A J 1998 *Nature* **392** 147
- [17] Iliev M N, Litvinchuk A P, Lee H G, Chu C W, Barry A and Coey J M D 1999 *Phys. Rev. B* **60** 33
- [18] Iliev M N, Litvinchuk A P, Lee H G, Chu C W, Barry A and Coey J M D 1999 *Phys. Status Solidi b* **215** 643
- [19] Cheng R, Borca C N, Dowben P A, Stadler S and Idzerda Y U 2001 *Appl. Phys. Lett.* **78** 521
- [20] Granado E, Moreno N O, Martinho H, Garcia A, Sanjurjo J A, Torriani I, Rettori C, Neumeier J J and Oseroff S B 2001 *Phys. Rev. Lett.* **86** 5385
- [21] Braden M, Hennion B, Reichardt W, Dhahlenne G and Revcolevschi A 1998 *Phys. Rev. Lett.* **80** 3634
- [22] Wang K Y, Spinu L, He J, Zhou W, Wang W and Tang J 2002 *J. Appl. Phys.* **91** 8204
- [23] Chen X K, Irwin J C and Frank J P 1995 *Phys. Rev. B* **52** R13130
- [24] Iliev M N, Litvinchuk A P, Lee H G, Chen C L, Dezaneti M L, Chu C W, Ivanov V G, Abrashev M V and Popov V N 1999 *Phys. Rev. B* **59** 364
- [25] Yu T, Shen Z X, Shi Y and Ding J 2002 *J. Phys.: Condens. Matter* **14** L613