

## Raman spectroscopy of ferromagnetic CrO<sub>2</sub>

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Polarized Raman spectra of the ferromagnetic metal CrO<sub>2</sub> were measured in a broad temperature range including  $T_c \approx 390$  K. The Raman-allowed modes of  $A_{1g}$ ,  $B_{1g}$ ,  $B_{2g}$ , and  $E_g$  symmetry were identified and compared to the corresponding modes of isostructural TiO<sub>2</sub>. The two low-frequency Raman lines are relatively narrow, indicating weak scattering of the corresponding  $B_{1g}$  and  $E_g$  phonons. Whereas the Raman intensities are not visibly affected by the magnetic ordering, the dependences on temperature of the phonon wave numbers exhibit peculiarities that could be attributed to a spin-phonon interaction. The variations with  $T$  of the phonon linewidths follow at low temperatures the dependence expected for phonon-phonon scattering. An additional broadening at higher temperatures with a maximum near  $T_c$  is tentatively assigned to scattering from collective spin fluctuations. [S0163-1829(99)00825-5]

Chromium dioxide, CrO<sub>2</sub>, has attracted significant interest as it has a unique electronic band structure, resulting in half-metallic ferromagnetism ( $T_c \approx 390$  K) with completely spin-polarized electrons at  $E_F$ .<sup>1-4</sup> Although there have been numerous reports on the magnetic, electric, and structural properties of CrO<sub>2</sub>, there are few data on its phonon spectra. Symmetry analysis of the zone-center phonons of CrO<sub>2</sub> (space group  $P4_2/mnm$ ) reveals that there are four Raman-active phonon modes of  $A_{1g}$ ,  $B_{1g}$ ,  $B_{2g}$ , and  $E_g$  symmetry and four infrared-active phonon modes ( $A_{2u} + 3E_u$ ).<sup>6</sup> The atomic motions corresponding to the Raman modes are shown in Fig. 1. Lewis *et al.*<sup>2</sup> predicted the frequency of the  $A_{1g}$  mode to be  $587 \text{ cm}^{-1}$ . Basov *et al.*<sup>7</sup> measured the optical conductivity in the infrared frequency range and found three peaks at  $357$ ,  $474$ , and  $573 \text{ cm}^{-1}$ , which should correspond to transverse optical phonons. No conclusion was drawn regarding the symmetry of these infrared-active vibrations.

In this work we report the polarized Raman spectra of CrO<sub>2</sub> as obtained from (110)- and (001)-oriented thin films on TiO<sub>2</sub> substrates of the same orientation. The Raman lines corresponding to the Raman-allowed phonon modes were unambiguously identified and their variation with temperature was studied between 5 and 420 K.

In the upper part of Fig. 2 are shown the Raman spectra of CrO<sub>2</sub> as obtained at 300 K with 632.8 nm laser excitation in four different scattering configurations,<sup>5</sup> namely,  $y'(x'x')\bar{y}'$  ( $A_{1g} + B_{2g}$ ),  $y'(zz)\bar{y}'$  ( $A_{1g}$ ),  $y'(zx')\bar{y}'$  ( $E_g$ ), and  $z(x'y')\bar{z}$  ( $B_{1g}$ ) scattering configurations ( $x'$ ,  $y'$ , and  $z$  correspond to the crystallographic directions  $[1\bar{1}0]$ ,  $[110]$ , and  $[001]$ , respectively; in the brackets are the allowed phonon mode symmetries). In the lower part of Fig. 2 the corresponding spectra for the isostructural compound TiO<sub>2</sub> are shown. The latter spectra are identical to those reported in the pioneering work of Porto *et al.*<sup>6</sup> Figure 3 shows the temperature evolution of the spectra of CrO<sub>2</sub> between 5 and 420 K. These spectra were obtained with 514.5 nm excitation from the

(110)-oriented film with incident polarization along  $x'$  and without an analyzer. Therefore they are a superposition of  $y'(x'x')\bar{y}'$  ( $A_{1g} + B_{2g}$ ) and  $y'(x'z)\bar{y}'$  ( $E_g$ ) spectra. In Table I are compared the wave numbers and linewidths of the Raman phonon lines of CrO<sub>2</sub> and TiO<sub>2</sub> at 300 K and 5 K as well as their relative intensities with 632.8 nm and 514.5 nm excitation. To calculate the relative intensities we fitted each phonon line by a Lorentzian and normalized its area to that of the  $A_{1g}$  line in the  $x'x'$  spectrum with the same excitation and at the same temperature.

It follows from Figs. 2 and 3 and Table I that the Raman spectra of CrO<sub>2</sub> and TiO<sub>2</sub> exhibit definite differences, namely, (i) only the one-phonon lines are pronounced in the spectra of CrO<sub>2</sub> in contrast to TiO<sub>2</sub>, where the intensity of two-phonon bands is comparable to that of the one-phonon lines; (ii) the  $A_{1g}$  and  $B_{2g}$  lines are of comparable intensity in CrO<sub>2</sub>, whereas in TiO<sub>2</sub> the  $B_{2g}$  line is weaker by two orders of magnitude; and (iii) the Raman line corresponding to the  $A_{1g}$  mode is of comparable intensity with  $xx(x'x')$  and  $zz$  scattering configurations for CrO<sub>2</sub>, whereas the  $zz$

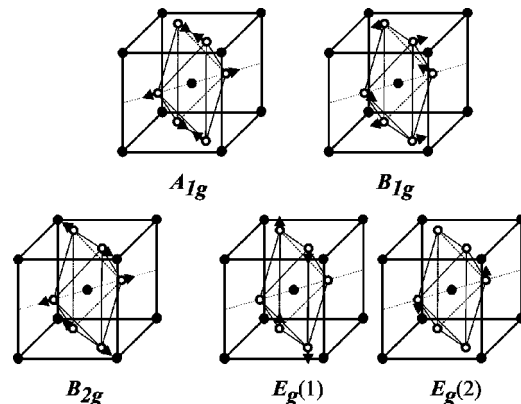


FIG. 1. Main atomic motions in the Raman modes of CrO<sub>2</sub> (space group  $P4_2/mnm$ ). Only oxygen atoms participate in these modes.

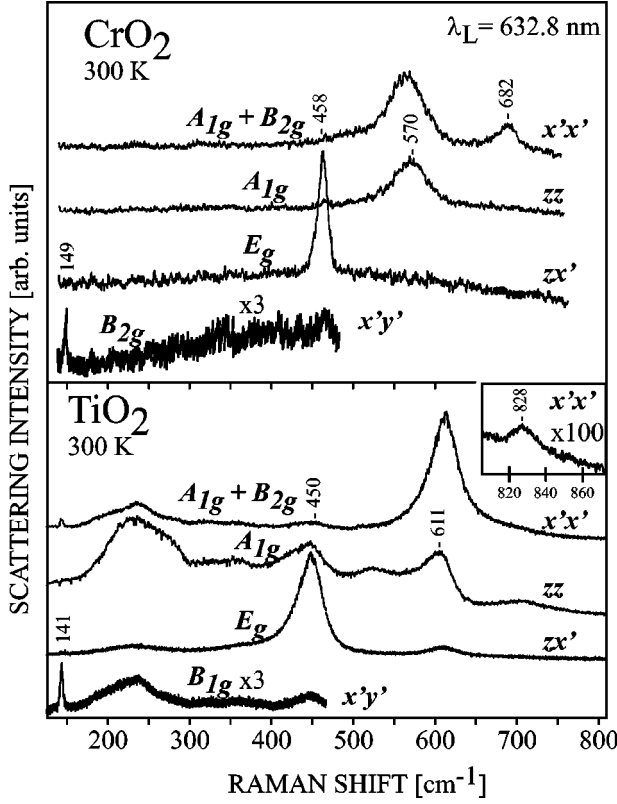


FIG. 2. Polarized Raman spectra of  $\text{CrO}_2$  and  $\text{TiO}_2$  as obtained at 300 K with 632.8 nm excitation.

component is much weaker in the case of  $\text{TiO}_2$ .

It is plausible to assume that the above differences in the otherwise isostructural compounds are due mainly to the different intermediate electronic states in the Raman scattering process.  $\text{TiO}_2$  is a transparent material and the laser excitation energies (1.96 and 2.41 eV) used in our experiments are well below the gap for electronic transitions. In contrast, upon photon excitation the final states of both spin-up and spin-down electrons in  $\text{CrO}_2$  are in the corresponding conduction bands.<sup>3,8</sup> The Raman-scattering efficiency  $\eta$  for a given phonon can be expressed as<sup>9</sup>

$$\eta = \left(\frac{\omega_s}{c}\right)^4 LV |\mathbf{e}_i \cdot \mathcal{R} \cdot \mathbf{e}_s|^2, \quad (1)$$

TABLE I. Wave number and halfwidth of the Raman phonon lines of  $\text{CrO}_2$  and  $\text{TiO}_2$  at 300 K and 5 K, and their relative intensities with 632.3 nm and 514.5 nm laser line excitation.

Raman mode	$T$ (K)	$\text{CrO}_2$			$\text{TiO}_2$		
		Position ( $\text{cm}^{-1}$ )	Width ( $\text{cm}^{-1}$ )	Intensity (632.8 nm)	Position ( $\text{cm}^{-1}$ )	Width ( $\text{cm}^{-1}$ )	Intensity (632.8 nm)
$A_{1g}$	5	574	24		612	21	
				1.00(xx)			
				1.61(zz)			
$A_{1g}$	300	570	49	1.00(xx)	611	44	1.00(xx)
				0.59(zz)			0.33(zz)
$B_{1g}$	5				144	3.5	
	300	149	3.0	0.01	141	3.7	0.006
$B_{2g}$	5	693	16				
	300	682	29	0.19	828	14.1	0.002
$E_g$	5	471	4.5		454	10	
	300	458	11.5	0.22	450	36	0.81

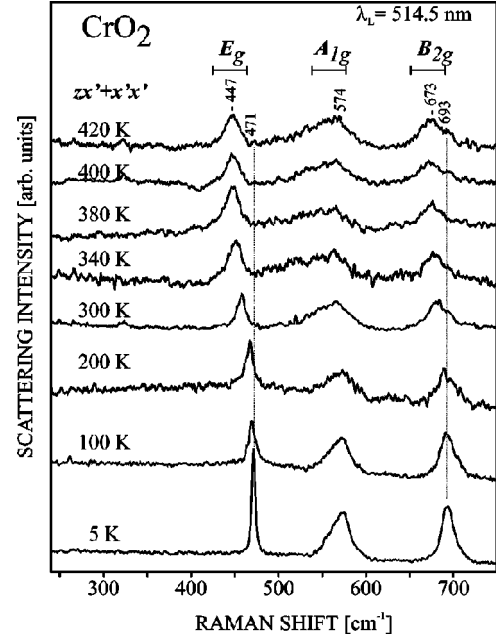


FIG. 3. Variations of the  $x'x' + x'z$  Raman spectrum of  $\text{CrO}_2$  between 5 and 420 K. The excitation photon energy was 2.41 eV (514.5 nm).

where  $i$  and  $s$  are indices for *incident* and *scattered* radiation,  $L$  is the *scattering length* defined for an absorbing material as  $(\alpha_i + \alpha_s)^{-1}$  ( $\alpha$  is the absorption coefficient),  $V$  is the volume of the sample producing the scattered radiation (for a parallel beam with area  $A$ ,  $V = LA$ ),  $\mathbf{e}_i$  and  $\mathbf{e}_s$  denote the incident and scattered polarization, and  $\mathcal{R}$  is the corresponding *Raman tensor*. For the transparent range the second-rank Raman tensor  $\mathcal{R}$  is defined as

$$\mathcal{R} = \mathcal{R}^{\omega_i, \Omega} = \left( \frac{\partial \chi}{\partial \mathbf{Q}} \right)_{\mathbf{Q}=0} \mathbf{Q}(\Omega), \quad (2)$$

where  $\mathbf{Q}(\mathbf{r}, t) = \mathbf{Q}(\mathbf{q}, \Omega) \cos(\mathbf{q} \cdot \mathbf{r} - \Omega t)$  are the atomic displacements associated with a phonon with wave vector  $\mathbf{q}$  and frequency  $\Omega$  and  $\chi(\mathbf{k}_i, \omega_i, \mathbf{Q}) = \chi(\mathbf{k}_i, \omega_i) + (\partial \chi / \partial \mathbf{Q})_0 \mathbf{Q}(\mathbf{r}, t) + \dots$  is the electric susceptibility. For photon energies within the range of direct interband elec-

tronic transitions, in particular near a critical point, the non-zero components of  $\mathcal{R}$  may significantly increase due to a strong modulation of combined electronic densities of states [and hence of  $\chi(\omega_i)$ ] by particular atomic vibrations. Despite the strong increase of  $\mathcal{R}$  in such resonance conditions, however, the scattering efficiency  $\eta$  of a light-absorbing medium as a whole decreases due to the much stronger effect of the reduced scattering length  $L$  and scattering volume  $V$ . The resonance conditions for  $\text{CrO}_2$  do change with variation of the excitation photon energy as manifested by the significant difference of the relative intensity of the  $B_{2g}$  mode with 632.8 and 514.5 nm excitation.

The resonant conditions (and hence of the relative Raman line intensities) are expected to change also for a fixed excitation photon energy provided the electronic structure undergoes changes. For ferromagnetic materials such changes could be induced by the spin ordering, resulting in a splitting of electronic bands into spin-polarized subbands. Such a magnetic-order-dependent Raman scattering has been reported, e.g., for the ferromagnetic semiconductors  $\text{CdCr}_2\text{Se}_4$  and  $\text{CdCr}_2\text{S}_4$  where some of the Raman lines increase strongly upon cooling below the corresponding Curie temperatures.<sup>10</sup> It has been shown that such a temperature behavior which is sensitive to the laser photon energy could be explained by the exchange splitting of the electronic bands resulting in a change of combined electronic densities of states near the energy of the laser excitation.<sup>11</sup>

It follows from Fig. 3, within the accuracy of our experiments, that no redistribution of the relative intensities of the Raman lines of  $\text{CrO}_2$  has been detected near  $T_c \approx 390$  K. This is an indication that the combined electronic density of states near 2.4 eV is not strongly affected by magnetic ordering. Such a result indicates that Hund's rule exchange splitting is still present up to the highest temperature in our experiments (420 K) and, therefore, the electronic structure of magnetically ordered domains above  $T_c$  is very similar to the one in the ferromagnetic phase below  $T_c$ .

The variations with temperature of the position the  $E_g$ ,  $A_{1g}$ , and  $B_{2g}$  Raman lines are shown in the right panels of Fig. 4. While with temperature increasing from 5 to 420 K the  $E_g$  and  $B_{2g}$  modes soften by 5.5% and 3%, respectively, the softening of the  $A_{1g}$  mode is less than 1%. As the experimental points are restricted to temperatures close to above  $T_c$ , no definite conclusion can be drawn about the effect of magnetic ordering on the phonon frequencies. Nevertheless, there are indications for anomalies near  $T_c$  in the position of both the  $A_{1g}$  and  $E_g$  modes.

The dependences of the phonon linewidth vs temperature,  $\Gamma(T)$ , are illustrated in the left panels of Fig. 4. At low temperatures the linewidth of the  $E_g$  phonon is relatively low ( $4.5 \text{ cm}^{-1}$ ). For the  $B_{1g}$  phonon, which was not measured at low temperatures,<sup>12</sup> an even smaller linewidth is expected as at 300 K its width is only  $3 \text{ cm}^{-1}$ , equal to the resolution of our spectrometer. The linewidth of a phonon line is a measure of the phonon scattering. The small widths of the low-frequency  $B_{1g}$  and  $E_g$  phonons, therefore, provide an evidence for a weak scattering. In contrast, the much higher linewidths of the  $A_{1g}$  and  $B_{2g}$  phonons ( $24 \text{ cm}^{-1}$  and  $16 \text{ cm}^{-1}$ , respectively, at 5 K) indicate that these phonons scatter much more strongly. This observation is consistent

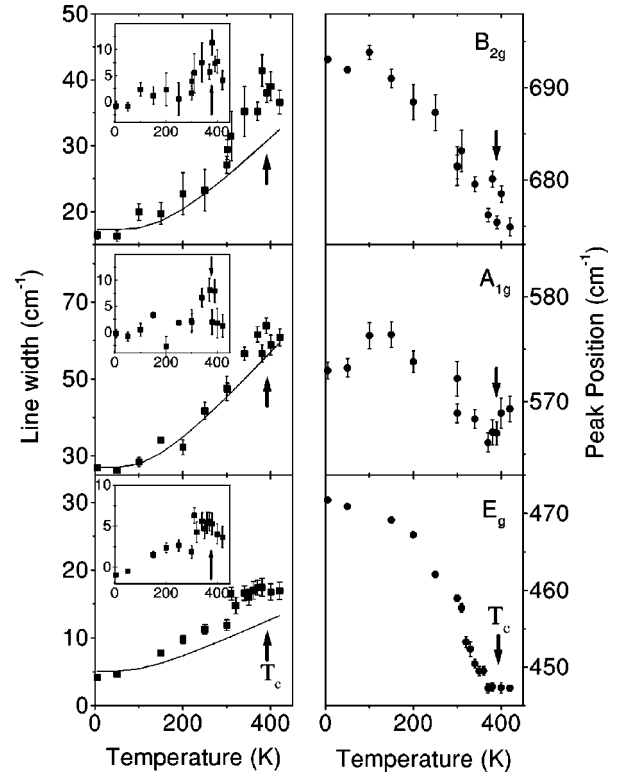


FIG. 4. Variations with temperature of the peak positions and linewidths of the  $E_g$ ,  $A_{1g}$ , and  $B_{2g}$  Raman lines of  $\text{CrO}_2$ . The solid lines in the left panels represent the corresponding functions  $\Gamma_{pp}$  which describe the phonon-phonon interaction. The insets show the additional broadening  $\Delta\Gamma = \Gamma_{\text{exp}} - \Gamma_{pp}$  assigned to magnetic scattering.

with the results of Basov *et al.*<sup>7</sup> who found that at low temperatures the electronic scattering below  $500 \text{ cm}^{-1}$  becomes negligible.

It is plausible to assume that the dependence  $\Gamma(T)$  is governed by mainly phonon-phonon scattering (anharmonic decay), described by

$$\Gamma_{pp}(T) = \Gamma_0 \left[ 1 + \frac{2}{\exp(\hbar\Omega/2k_B T) - 1} \right], \quad (3)$$

where  $\Gamma_0$  is the linewidth at  $T=0$  and  $\Omega$  is the phonon frequency. The function  $\Gamma_{pp}(T)$ , shown by solid curve in the left panels of Fig. 4, fits satisfactorily the experimental points at low temperatures. At high temperatures, however, the experimental points lie above  $\Gamma_{pp}(T)$ , indicating that another channel could also be involved in the scattering process. For a magnetic material like  $\text{CrO}_2$  such an additional channel could arise from scattering from the collective spin fluctuations (spin disorder scattering) that exist near  $T_c$ . If so, the contribution of spin-disorder scattering to the phonon linewidth should pass over a maximum near  $T_c$ . The differences  $\Delta\Gamma = \Gamma_{\text{exp}} - \Gamma_{pp}$ , shown in the insets of Fig. 4, do have a maximum near  $T_c$ , although a more definite conclusion could be drawn only after extending the measurements to higher temperatures. It is worth noting here that the local

maximum near  $T_c$  of the phonon linewidth has recently been reported for another ferromagnetic compound, SrRuO<sub>3</sub>, which is also a “bad” metal.<sup>13</sup>

In conclusion, we measured the polarized Raman spectra of ferromagnetic metal CrO<sub>2</sub> in a broad temperature range including  $T_c$  and identified all four allowed Raman modes. The low-frequency Raman lines of  $B_{1g}$  and  $E_g$  symmetry are very narrow, indicating weak phonon scattering, in particular at low temperatures. The Raman intensities are not strongly affected by the magnetic ordering, whereas the line position

vs  $T$  dependences change their slope near  $T_c$  for the  $A_{1g}$  and  $E_g$  modes. At low temperatures the variations with  $T$  of the phonon linewidths follow the dependence expected for a phonon-phonon scattering. The additional broadening which appears with approaching  $T_c$  is tentatively assigned to the scattering of phonons from collective spin fluctuations.

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<sup>1</sup>K. Schwarz, J. Phys. F **16**, L211 (1986).

<sup>2</sup>S.P. Lewis, P.B. Allen, and T. Sasaki, Phys. Rev. B **55**, 10 253 (1997).

<sup>3</sup>M.A. Korotin, V.I. Anisimov, D.I. Khomskii, and G.A. Sawatzky, Phys. Rev. Lett. **80**, 4305 (1998).

<sup>4</sup>R.J. Soulen, Jr., J.M. Byers, M.S. Osofsky, B. Nadgorny, T. Ambrose, S.F. Cheng, P.R. Broussard, C.T. Tanaka, J. Nowak, J.S. Moodera, A. Barry, and J.M.D. Coey, Science **282**, 85 (1998).

<sup>5</sup>For the scattering configuration we use the  $a(bc)d$ -type (Porto's) notation, where  $a$  and  $d$  are the directions and  $b$  and  $c$  are the polarization of the incident and scattered light, respectively.

<sup>6</sup>S.P.S. Porto, P. A. Fleury, and T.C. Damen, Phys. Rev. **154**, 522 (1967).

<sup>7</sup>D. N. Basov, E. J. Singley, C. P. Weber, A. Barry, and J. M. D. Coey (unpublished).

<sup>8</sup>I.I. Mazin, D.J. Singh, and Claudia Ambrosh-Draxl, Phys. Rev. B **59**, 411 (1999).

<sup>9</sup>Peter Y. Yu and Manuel Cardona, *Fundamentals of Semiconductors* (Springer-Verlag, Berlin, 1996).

<sup>10</sup>G. Harbeke and E.F. Steigmeier, Solid State Commun. **6**, 747 (1968); E.F. Steigmeier and G. Harbeke, Phys. Kondens. Mater. **12**, 1 (1970).

<sup>11</sup>M. Iliev, G. Güntherodt, and H. Pink, Solid State Commun. **27**, 863 (1978).

<sup>12</sup>In our low-temperature measurements we used an (110)- oriented film, where no scattering configurations for observation of the  $B_{1g}$  mode were available.

<sup>13</sup>M.N. Iliev, A.P. Litvinchuk, H.-G. Lee, C.L. Chen, L.M. Dezaneti, C.W. Chu, V.G. Ivanov, M.V. Abrashev, and V.N. Popov, Phys. Rev. B **59**, 364 (1999).