Raman studies of nearly half-metallic ferromagnetic CoS$_2$

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Abstract

We measured the Raman spectra of ferromagnetic, nearly half-metallic, CoS$_2$ over a broad temperature range. All five Raman active modes $A_g$, $E_g$, $T_g$(1), $T_g$(2) and $T_g$(3) were observed. The magnetic ordering is indicated by a change of the temperature dependences of the frequency and the line width of $A_g$ and $T_g$(2) modes at the Curie point. The temperature dependence of the frequencies and line widths of the $A_g$, $E_g$, $T_g$(1), $T_g$(2) modes in the paramagnetic phase can be described in the framework of the Klemens approach. Hardening of the $T_g$(2), $T_g$(1) and $A_g$ modes on cooling can be unambiguously seen in the ferromagnetic phase. The line widths of $T_g$(2) and $A_g$ modes behave in a natural way at low exciting laser powers (they decrease with decreasing temperature) in the ferromagnetic phase. At high exciting laser powers the corresponding line widths increase as temperature decreases below the Curie temperature. Then, as will be shown, the line width of the $A_g$ mode reaches a maximum at about 80 K. Tentative explanations of some of the observed effects are given, taking into account the nearly half-metallic nature of CoS$_2$.

Keywords: Raman scattering, half metal, CoS$_2$

(Some figures may appear in colour only in the online journal)

1. Introduction

Cobalt disulphide, CoS$_2$, a metallic compound with the cubic pyrite-type crystal structure [1], experiences a phase transition to a ferromagnetic state at $T_c \approx 122$ K [2]. The magnetic and electric properties verify the itinerant nature of magnetism in CoS$_2$ [2–6]. Upon entering the ferromagnetic state CoS$_2$ becomes a nearly half-metal with a significant decrease in the density of states at the Fermi level that is reflected in an increase in the resistivity below $T_c$ [7, 8]. An influence of half-metallicity on the thermodynamic properties and phase diagram of CoS$_2$ was reported in [9]. So one might expect that the lattice dynamic of CoS$_2$ should somehow reveal this effect as well. On the other hand the connection between the anomalous behavior of some optical modes, observed in a Raman study of the model half-metal CrO$_2$ and half-metallicity, was not recognized [10]. In the present paper we report a detailed Raman study of single crystals of CoS$_2$ in the temperature range 10–500 K. Earlier Raman scattering studies of CoS$_2$ at temperature 300 K were carried out in [11, 12]. We conclude that the half-metallic state strongly modifies the ion–ion interaction in CoS$_2$ that therefore influences the stretching modes in the ferromagnetic phase.

As was mentioned, the crystal structure of CoS$_2$ belongs to the pyrite type, space group Pa3, with four formula units per unit cell. The Co atoms are situated on the sites of a face-centered cubic lattice whereas the S atoms are grouped in dumb-bell pairs oriented along the [1 1 1] direction and located in the center of the cell and the midpoints of the cell edges, as is shown in figure 1.

Five Raman modes $A_g$, $E_g$, $T_g$(1), $T_g$(2) and $T_g$(3), as identified by group theory analysis [13, 14], can be active in the CoS$_2$ structure and all of them were observed in the current experiments. The $A_g$ and $T_g$(2) modes correspond to the in-phase and out-of-phase stretching vibrations of sulfur atoms in the dumb-bells. $E_g$ is a pure librational mode of the dumb-bells, whereas $T_g$(1) and $T_g$(3) modes correspond to various combinations of stretching and librational vibration.
2. Experimental

Raman measurements were performed using a 488 nm \( \text{Ar}^+ \) laser line for excitation and a triple-grating spectrometer (Princeton Instruments TriVista 555) with a liquid-nitrogen cooled Charge Coupled Device-silicon based multichannel array detector (CCD). Measurements in the temperature range 80–300 K were performed with a micro-Raman setup: the samples were placed inside a cryostage (Linkam THMS600) and the 50\( \times \) objective of an Olympus BX51 microscope was used to focus the laser and collect the Raman signal. The laser spot on the sample inside the cryostage was less than \( \sim 1–2 \mu \text{m} \) in diameter. Measurements in the 10–300 K range were carried out making use of a He cryostat (Oxford Instruments OptistatSXM) and achromatic lenses were used for focusing and collecting the signal. The laser spot on the sample inside the cryostat was less than \( \sim 5–10 \mu \text{m} \). In order to avoid overheating of the samples the laser power was kept at its minimum: \( \sim 1 \) mW was measured at the entrance window of the cryostage and \( \sim 7 \) mW at the front window of the cryostat.

In both optical setups the true backscattering configuration was used. Polarized spectra were measured in the HH (i.e. the incident and scattering polarizations are parallel) and the HV (i.e. the incident and scattering polarizations are perpendicular) configurations. The spectral slit width was less than \( 3 \) cm\(^{-1} \).

Single crystals of CoS\(_2\) were grown in the Ames Laboratory according to the chemical vapor transport procedure used by Wang et al [15]. The crystals that resulted following the two-week growth run had dimensions of 1 mm or less. The crystals have a cubic pyrite-type structure with a lattice parameter \( a = 5.5362\pm0.0002 \) Å. The crystal quality is characterized by their high residual resistivity ratio, \( \text{RRR} = \rho_{297K}/\rho_{2K} = 285 \), which is the highest reported so far for CoS\(_2\) [16].

The measurements were performed making use of three samples of CoS\(_2\), hereafter designated as samples A, B and C.

3. Results

A general view of the Raman spectra of CoS\(_2\) is presented in figures 2(a) and (b). To analyze the temperature evolution of the Raman modes, the corresponding peaks were approximated by a combination of the Lorentzians that were fitted in each case. We did not apply more complicated approximations because the spectral width of the spectrometer slit was much smaller (3 cm\(^{-1} \)) than the half-widths of the measured lines (8 cm\(^{-1} \)).

Figure 3 (left panel) illustrates some features of the spectra evolution (frequencies and line widths), measured in geometries HH and HV in a micro-Raman cryostage. The data shown in figure 3 (right panel) were obtained in a helium cryostat.

The temperature dependence of the frequencies and half-widths of the Raman modes \( E_g, T_g(1), A_g, T_g(2) \) using high intensity laser excitation (7.5 mW at the window of the Lincam...
Figure 3. Frequencies and line widths (FWHM-full width at half maximum) as a function of temperature for $E_g$, $T_g(1)$, $A_g$ and $T_g(3)$ modes in sample A at high power (7.5 mW) laser excitation. Data for the $E_g$ and $A_g$ modes are from the HH configuration. Data for $T_g(1)$ and $T_g(3)$ modes are obtained in the HV configuration, where these modes are more pronounced. Solid lines are the least-square fitting of data taken above $T_c = 122$ K with expressions derived in the framework of the Klemens approach [17–19]. However, because this approach cannot be fully justified in the case of conductive materials, these lines may serve as a guide to the eye.

cryostage) for sample A is shown in figure 3. The continuous lines in figure 3 represent the results of the approximation of the data corresponding to the paramagnetic phase of CoS$_2$ by the expressions describing the temperature dependence of the frequencies and half-widths of the Raman modes in CoS$_2$, in the spirit of the model of the decay of optical phonons developed by Klemens and others (see [17–19]). The Klemens model assumes that the Raman phonon decays into two acoustic phonons of opposite wave vectors that belong to the same branch in the phonon dispersion curve. These ‘three phonon’ expressions seem to work satisfactorily in the paramagnetic phase, though one cannot be sure that the Klemens approach is completely applicable in the case of metallic crystals. The electron–phonon interaction may contribute significantly to the light scattering.

As is seen in figure 3 the measured frequencies and half-widths of the Raman modes, possibly with the exception of the frequency of $E_g$ mode and half-widths of $T_g(1)$ and $E_g$ modes, experience some anomalies at the Curie point. The behavior of the frequencies of $A_g$, $T_g(2)$ modes in the ferromagnetic phase seem to be a natural result of mode softening in the vicinity of the phase transition. On the other hand the increase of the width of the $T_g(2)$ and $A_g$ modes with decreasing temperature appears to be counterintuitive. Note that such an effect was discovered previously in the Raman studies of CoF$_2$ and still lacks an explanation [20]. As we will see, at low power excitation the width of the corresponding modes behaves in a natural way—it decreases with decreasing temperature.

The temperature dependence of the frequencies, widths and intensities of $A_g$ and $E_g$ modes for sample C at two different laser beam powers is displayed in figure 4. As can be seen in figure 4 the temperature dependencies of frequency, width and intensity of the $E_g$ mode, which is related to a pure librational motion of the sulfur dumb-bells, do not exhibit anomalies at the Curie point at either laser power. At the same time the $A_g$ mode, corresponding to the in-phase stretching vibrations of sulfur atoms in the dumb-bells, shows both a clear anomaly at the Curie point and an obvious sensitivity to the excitation power. As is shown in figure 5 the temperature dependence of the $A_g$ frequency at low excitation power
reveals a sharp turn at \( T_c \approx 122 \text{ K} \), indicating the existence of a well-defined second-order phase transition (no discontinuity is observed). But at increased laser power the phase transition features are slightly smeared out, probably due to a temperature gradient arising as a result of overheating the sample. At the same time, the width of the \( A_g \) peak experiences a drastic change with increased power, as illustrated in figure 4. The abnormal behavior of the width of the \( A_g \) peak (its width increasing with decreasing temperature) is probably closely related to these factors, which define the smearing out of the phase transition. Note also that the \( A_g \) and \( E_g \) peak intensities are not influenced by the phase transition and temperature (figure 4).

Figure 5 shows the temperature dependence of the \( A_g \) mode frequencies and line widths at low and high laser power excitation for samples A (left panel) and B (right panel). The left panel data differ little from the data in figure 4, though they probably show that high intensity excitations decrease the frequencies of the \( A_g \) mode in the paramagnetic phase. In the right panel of figure 5 the data obtained in the extended temperature range in a helium cryostat are shown. These data unambiguously demonstrate that the \( A_g \) line-width increase observed in the ferromagnetic phase does not continue to the lowest temperatures but reaches its maximum at \( T_c \approx 80 \text{ K} \). This non-trivial feature is probably connected with a mechanism of the optical phonon decay in the ferromagnetic phase of \( \text{CoS}_2 \). We will briefly discuss this matter in the following section.

Figure 6 illustrates that the frequency and the line width of the \( A_g \) mode in the ferromagnetic phase are more sensitive to the variation of the excitation power than the same quantities in the paramagnetic phase, which obviously results from the magnetic order response to the sample heating.

4. Discussion

Before proceeding to the discussion let’s shortly summarize the main findings of the current paper.

All five Raman active modes \( A_g, E_g, T_g(1), T_g(2) \) and \( T_g(3) \) (see figure 2) were observed in single crystals of the itinerant ferromagnet \( \text{CoS}_2 \). The temperature dependence of the frequencies and line widths of the \( A_g, E_g, T_g(1), T_g(2) \), modes in the paramagnetic phase can be described in the framework of
Figure 5. Temperature dependence of the $A_g$ mode frequencies and line widths at low and high laser power excitation: left panel shows results of micro-Raman studies of the sample A in the 80–300 K range; right panel shows Raman studies of the sample B in the range 10–300 K. Solid lines are a guide to the eye.

the Klemens approach [17–19] (figure 3). In the ferromagnetic phase, the $T_g(2)$, $A_g$, and $T_g(1)$ modes reveal distinct hardening on cooling as is seen in figure 3. The behavior of the $A_g$ mode indicates a smearing out of the phase transition at high excitation power (figure 4) that possibly arises from a temperature gradient in the sample. The line widths of $T_g(2)$ and $A_g$ modes behave in an expected way at low laser excitation power (they decrease with decreasing temperature) in the ferromagnetic phase (figures 4 and 5); but at high laser excitation power the corresponding line widths increase with a decrease in temperature below $T_c$. But then, as can be seen in figure 5, the line width of the $A_g$ mode reaches a maximum at about 80 K. At this point it should be mentioned that a number of studies of spin ordering effects on the lattice dynamics in various substances always indicate strong changes of the phonon frequency and line width of all or selected modes with variation of temperature (the hardening of optical phonons on cooling is common). As examples we can refer to the Raman and some IR studies of ferromagnetic semiconductors CdCr$_2$Se$_4$ and CdCr$_2$S$_4$ [21], the ferromagnetic metal La$_{0.7}$Ca$_{0.3}$MnO$_3$ [22], the strongly correlated ferromagnetic metal SrRuO$_3$ [23], the half-metal CrO$_2$ [10], antiferromagnetic halides of transition metals [24] and the antiferromagnetic metal $\alpha$-MnSe [25]. As seen in the cited references quite different explanations have been suggested for the observed effects. So far no general mechanism has been identified. As for the case of CoS$_2$, L. Falkovsky in a recent paper [26] interpreted some of our data on the Raman scattering in CoS$_2$ more or less successfully in terms of the phonon–electron interaction, arising from interband transitions at finite temperature. As Falkovsky’s analysis shows the expected direct phonon–magnon interactions are unable to contribute significantly to the observed effects. Note that according to the theory [26] the phonon–electron interactions in CoS$_2$ influence the line shift and width both in the ferromagnetic and paramagnetic phases.

Unfortunately we are unable in the framework of the current paper to analyze in details the Raman scattering and IR studies in magnetic substances. Instead we will briefly review the relevant experimental data on the above-mentioned ferromagnetic metal La$_{0.7}$Ca$_{0.3}$MnO$_3$ [22], the strongly correlated ferromagnetic metal SrRuO$_3$ [23] and the ferromagnetic half-metal CrO$_2$ [10].

In case of La$_{0.7}$Ca$_{0.3}$MnO$_3$, infrared reflectivity studies show that the bending and stretching modes of the MnO$_6$ octahedra reveal significant frequency shifts (hardening on cooling) below the Curie temperature $T_c$. At the same time the lattice constant of La$_{0.7}$Ca$_{0.3}$MnO$_3$ demonstrates a negative anomaly below $T_c$, which may indicate the magnetovolume effect as at least partially responsible for the observed frequency shifts. Alternatively, Kim et al [22] proposed that the IR phonon hardening originates from a strong electron–phonon coupling and a crossover from small to large polaronic states. We note that the thermal expansion coefficient of La$_{0.7}$Ca$_{0.3}$MnO$_3$ experiences a positive shift at the phase transition on cooling that determines a positive slope $dT/dP$ of the phase transition line at high pressures.

The situation with a strongly correlated ferromagnetic metal SrRuO$_3$ is quite different. A jump of the thermal expansion coefficient of SrRuO$_3$ at the Curie point is negative [27], which implies that the volume of the system below $T_c$ decreases with temperature more slowly than it does in the paramagnetic phase. Nevertheless, all the studied Raman modes in SrRuO$_3$ demonstrate significant hardening on cooling, which clearly results from an enhancement of the
effective force constants in the ferromagnetic state. Authors of [23] hypothesize that the pronounced phonon hardening below \( T_c \) in SrRuO\(_3\) is determined to a great extent by an increase of the concentration of the free charge carriers upon cooling due to the delocalization of some electronic (or polaronic) states, though no real mechanism has been suggested.

The case of the model half-metallic ferromagnet CrO\(_2\) is somewhat special, because no noticeable volume anomaly at the phase transition was observed [28], though the high pressure studies indicate the existence of a negative jump of the thermal expansion coefficient at the phase transition [29]. At least one of the Raman modes of CrO\(_2\) shows hardening on cooling, but researchers have not suggested any particular explanation for this feature.

However, it seems to be clear that a spin ordering in all described cases modifies the electron structure of the materials in a way that enhances the electron–phonon interaction and therefore influences the phonon frequencies and corresponding line widths. Nevertheless the detailed mechanism of this complicated process can be different in various materials.

We turn again to the case of CoS\(_2\). The point here is that most of the electrons of the minority band become localized in the magnetic nearly half-metallic state of CoS\(_2\) with a general decrease of the electronic density of states. This leads to an enhancement of the direct Coulomb ion–ion repulsive interactions due to the decreased screening ability of the electronic gas and the influences of the stretching modes of the vibrational spectra of CoS\(_2\). A decrease of the compressibility and electronic heat capacity in the ferromagnetic phase of CoS\(_2\) supports the above conclusion [9]. Note that a decrease of compressibility is also observed in the ferromagnetic half-metallic phase of CrO\(_2\) [30].

The decay mechanism in the ferromagnetic phase of CoS\(_2\) certainly includes the Klemens anharmonic contribution. At the same time the optical phonons, as well as the other thermal excitations, could directly or indirectly turn over the spins in the majority band, therefore filling out the minority band in CoS\(_2\). This action defines another channel of the decay in the ferromagnetic phase. The maximum in the \( A_g \) line width at high laser power excitation (see figures 4 and 5) probably implies that this channel becomes less efficient in the vicinity of the phase transition.

5. Conclusion

In conclusion, we have measured the Raman spectra of ferromagnetic nearly half-metal CoS\(_2\) over a broad temperature range. The magnetic ordering is signified by a change of the temperature dependences of the frequency and the line width of \( A_g \) and \( T_g(2) \) modes at the Curie point. The Raman intensities are not practically affected by the magnetic ordering. Variations of frequencies of the Raman stretching modes in the ferromagnetic phase of CoS\(_2\) are defined solely by the modified ion–ion interaction, which is altered due to the nearly half-metallic character of the phase. This situation ceases to
exist above the Curie point and it is plausible that the Klemens anharmonic approach is valid in the paramagnetic phase. The latter seems to be supported by the experiment (figure 7). In figure 7 the temperature dependencies of the $A_g$ modes of CoS$_2$ and FeS$_2$ are compared. As is seen the Klemens approach works satisfactorily for FeS$_2$ and for the paramagnetic phase CoS$_2$, which confirms our supposition.

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