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Resonance Raman scattering in $CdCr_2S_4$: Magnetic-circular-polarization properties

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Spin-dependent (SD) phonon Raman scattering of $CdCr_2S_4$ is studied using a circularly polarized beam of a He-Ne (632.8-nm) laser in the Faraday configuration. It is found that magnetic-circular-polarization effects on the SD scattering are due to resonance with the "red-shifting" transitions in this ferromagnetic spinel. Anomalous temperature dependences of the Raman intensity for specific phonon lines E (351 cm^{-1}) and F (394 cm^{-1}) are explained by a phenomenological model which takes account of both resonance and magnetic-ordering effects for the scattering process. The mechanism for SD resonance scattering is shown to be closely connected to the absorption process which depends on magnetic ordering. Various models for the red-shifting transitions are discussed in the light of the present resonance Raman-scattering results for this ferromagnetic semiconductor.

I. INTRODUCTION

The chromium chalcogenide spinels ACr_2X_4 (A = Cd, Hg; x = S, Se) are well-known ferromagnetic semiconductors which have unique optical and transport properties associated with magnetic ordering.[1] They have been studied intensively during the last decade because of intriguing phenomena due to strong correlation between the electronic and spin subsystems.[1–3] The "red-shift" phenomenon of the absorption edge and the large negative magnetoresistance effects are especially interesting problems in these compounds.[1–3]

Spin-dependent (abbreviated as SD) phenomena in the Raman spectra were first observed by Steigmeier and Harbeke.[4] There are five first-order phonon lines in the Raman spectra of $CdCr_2X_4$, and the intensities of certain lines are found to increase below the magnetic ordering temperature.[4] Since the temperature dependence of the intensities varies like the spin-correlation function $\langle \vec{S}_i \cdot \vec{S}_j \rangle$, this effect is called SD phonon Raman scattering. Several models have been proposed to explain this phenomenon: One is a model which involves the ion-position dependence of the magnetic exchange interaction that couples the spin system and the phonons[5]; on the other hand, Suzuki and Kamimura formulated a general theory of phonon scattering in magnetic crystals and interpreted the SD phenomena as being due to the variation of the d-electron transfer energy with lattice vibrations and/or nondiagonal exchange interactions.[6]

Recently, we have studied the SD phenomena by using various wavelengths of excitation light and found the following facts[7–10]: (i) Prominent SD effects on certain phonon lines are observed with the excitation energies corresponding to the "red-shifting" (abbreviated as RS) transitions and strong band-to-band transitions in $CdCr_2X_4$ (X:S,Se).[7,8] (ii) Large magnetic-circular-polarization and magnetic field effects are observed in the Faraday configuration when $CdCr_2S_4$ is excited by red exciting light at low temperatures below T_C. (iii) The breakdown of selection rules for the polarization property is striking for the SD phonon lines.[4,8] From these results, we pointed out the important role of the resonance effect on the SD phenomena; the electronic states in resonance are strongly affected by magnetic ordering. It was difficult, however, to gain deeper understanding of these phenomena because of the ambiguous knowledge of the relevant electronic transitions in this system.

In this paper, we report on the study of resonance Raman effects with the RS transitions of $CdCr_2S_4$ measured by using circularly polarized light in the Faraday configuration. Circularly polarized light was adopted because two RS transitions C and A_2 are allowed for the right-circular polarization RCP(+) and the left-circular polarization LCP(−), respectively.[11] The following results have been obtained: The temperature dependences of the intensities for the SD lines are quite different for RCP and LCP, and they are interpreted by a postulated phenomenological model which takes account of the resonance effect with the RS transitions whose absorption coefficient increases near and below the Curie temperature $T_C = 84$ K. We find that the familiar spin-correlation-type temperature dependence[4] could be accidentally observed for linearly polarized or unpolarized light of a He-Ne laser at 632.8 nm.

In interpreting our results, resonance Raman scattering is seen as a two-photon process which consists of the absorption of the incident photon followed by "hot luminescence".[12–14] According to Falicov *et al.*[12,13] and Klein,[14] the intensity of resonance scattering is proportional to the product of the absorption coefficient and some relaxation factors in a single-resonant process when only one electronic transition is involved in the resonant-scattering process. Comparing the temperature dependence of the SD scattering intensity with that of the contribution of the RS peaks to the absorption coefficient at 632.8 nm, we find similar dependences between them. This means that the mechanism for the SD phonon Raman scattering arises mainly from the resonance effect of specific electronic transitions affected by magnetic ordering. In Sec. II, the experimental method is described, and the results will be explained in Sec. III. Section IV is devoted to an analysis and discussion of these results in relation to the origin of the RS transitions.

II. EXPERIMENTAL

Single crystals of $\mathrm{CdCr_2S_4}$ grown by a chemical-vapor transport method were used for the present Raman-scattering measurements. The plane (001) perpendicular to one of the easy-magnetization axes was polished to a mirrorlike surface with alumina powder (0.05 μm). The experimental setup is shown schematically in Fig. 1. All the measurements were controlled by a minicomputer (DEC PDP-11).[15] The main feature of this system is the capability for measuring several morphic effects.[15] We observed here circular-polarization effects of Raman scattering by using a quarter-wave plate whose rotation angle is controlled by the minicomputer. Scattered photon counts for right- and left-circularly polarized light are stored in two memories at each monochromator step corresponding to a Raman shift. Since the two photon counts are obtained under identical conditions, this method is effective in obtaining the difference of Raman signals for the two circularly polarized light beams. The linearly polarized light of a He-Ne laser (Spectra Physics 125) at 632.8 nm was converted into circularly polarized light by a quarter-wave plate which can be rotated by 90° under computer control. The laser beam of approximately 20 mW was focused onto the crystal surface. The temperature of the laser spot is expected to be higher than that of the bulk crystal. Bulk temperatures were measured by germanium and platinum resistors. The temperature difference between the laser spot and the bulk was about 15 K at 20-mW irradiation. This difference was estimated by using both the bulk temperature dependence and the laser power dependence of the scattered light intensity around T_C.

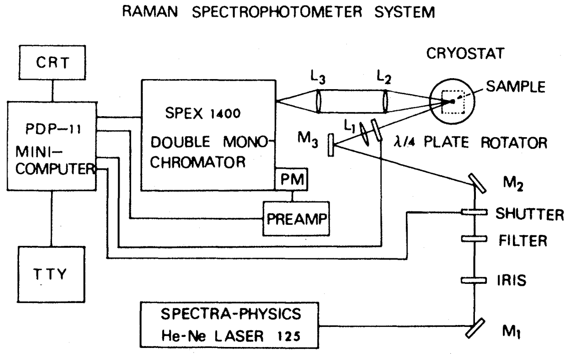

FIG. 1. Experimental setup for the present Raman-scattering measurements.

A single crystal (3 × 2 × 0.5 mm^3) pasted on a permanent magnet $\mathrm{SmCo_5}$ (8 mm diam × 6 mm) was fixed on the sample holder of a temperature variable metal cryostat. The crystal was cooled down to about 20 K through thermal conduction by liquid-He refrigerant. A magnetic field of 2.2 kOe which is strong enough to make a single-domain state was applied parallel to the [001] axis. Though the direction of the incident beam is slightly tilted (about 15°) from this axis, the propagation vector of the light inside the crystal is almost parallel to the magnetization direction (Faraday configuration) since the light beam is bent when it enters a refractive medium. The scattered light was analyzed using left- and right-circularly polarized sheets (Polaroid Co.) and was detected by a conventional double monochromator (Spex 1400) and a cooled photomultiplier (RCA C31034A) with a high quantum efficiency in the red. After the photocurrent pulses pass through a pulse-height discriminator, they are counted, and the count numbers are stored in the computer memory. The spectrum is displayed on a CRT scope and plotted by a teletype. The Raman signal was integrated for a sufficiently long time to obtain the necessary level of the signal-to-noise ratio.

III. EXPERIMENTAL RESULTS

It is known that $\mathrm{CdCr_2S_4}$ has the normal spinel structure with space-group $Fd3m$. According to group-theoretical analyses for the spinel structure with two molecular units in the primitive cell, there are 42 phonon modes out of which 12 are Raman active at $\vec{k}=0$. As for the polarization properties, one A_{1g} and one E_g modes are allowed for the diagonal polarization configuration, and three T_{2g} modes for the off-diagonal configuration in the Raman-scattering selection rule.[16] The Stokes Raman spectrum of $\mathrm{CdCr_2S_4}$ consists of five first-order phonon lines and several second-order lines. The frequencies and mode assignments of the first-order lines are as follows at room temperature[4]: A (101 cm^{-1}, T_{2g}), C (256 cm^{-1}, E_g), D (280 cm^{-1}, T_{2g}), E (351 cm^{-1}, T_{2g}), and F (394 cm^{-1}, A_{1g}). The assignment of the phonon modes were made on the basis of polarization properties,[4,8] lattice-dynamical studies,[17] and a comparison with the spectra of nonmagnetic $CdIn_2S_4$.[18] It was found that the breakdown of the polarization selection rule occurs under resonance conditions at low temperatures.[8] For instance, lines *E* and *F*, which show a prominent SD effect with red exciting light, are equally observed in both the diagonal and the off-diagonal polarization configurations below T_C.[8]

Among the five first-order lines, four lines except for line *C* show SD effects for the 632.8-nm excitation light.[4] The Stokes Raman spectra of $CdCr_2S_4$ in the four circular polarization configurations are shown in Fig. 2. We found the following results: The two spectra in the configurations (+, −) and (−, +) are different at 94 K (slightly above T_C) even though the two configurations are equivalent if the magnetization vector is not taken into account. The same kind of result has already been reported by Koshizuka *et al.*[9,10] for other excitation wavelengths of light near 632.8 nm. They confirmed that the spectrum for the configuration (+, −) transfers to that for the configuration (−, +) under the reversal of magnetization with 647.1-nm light.[9] Therefore, this phenomenon is clearly related to the SD effect of phonon Raman scattering. This anomaly is observed around the Curie temperature with 632.8-nm light, but it disappears at lower temperatures around 47 K, as shown in Fig. 2. This circular polarization effect originates from the resonance Raman effect, and the reason will be explained later.

In order to make certain that the circular polarization property is due to the resonance effect, the temperature dependence of the Raman spectra was measured without an analyzer for the scattered light. Figure 3 shows the spectra for the lines *E* and *F* at various temperatures, where both RCP and LCP spectra were measured in the same run. Such a large change of intensity is not observed for other phonon lines for the excitation wavelength near 632.8 nm. The difference between RCP and LCP spectra is extremely large near the ordering temperature as seen in Fig. 3.

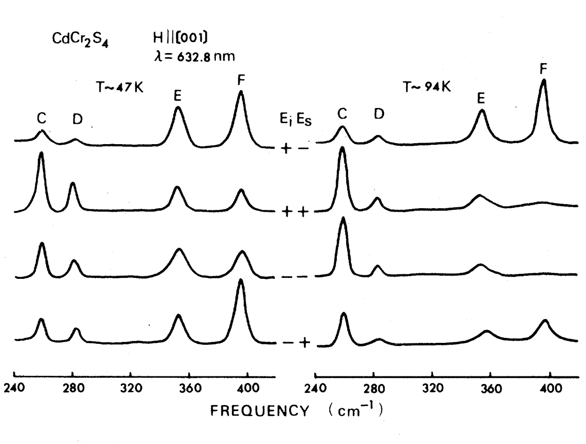

FIG. 2. Stokes Raman spectra of $CdCr_2S_4$ with various circular-polarization configurations at $T \cong 47$ and 94 K. The applied field is 2.2 kOe.

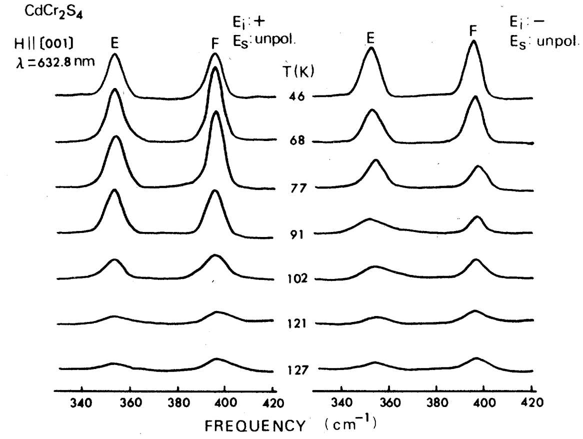

FIG. 3. Temperature dependences of Raman spectra of $CdCr_2S_4$ with right(+)- and left(−)-circularly polarized light. The scattered light is not analyzed. The applied field is 2.2 kOe.

The temperature dependences of the peak photon counts of lines *E* and *F* are shown in Fig. 4. The open and solid circles indicate the experimental values of line *E* for RCP and LCP, respectively, and similarly, the squares are for those of line *F*. In the case of RCP, the peak counts of both lines *E* and *F* start to increase slightly above T_C and reach the maximum at about 75 K. On the other hand, in the LCP case, the peak intensity increases below T_C like the temperature dependence of magnetization. In previous papers on SD Raman scattering, spin-correlation function-type behaviors were reported on the temperature dependence of the intensities for these lines for 632.8-nm (Ref. 4) and 647.1-nm (Refs. 7 and 8) unpolarized excitation light. It is easy to see in Fig. 4

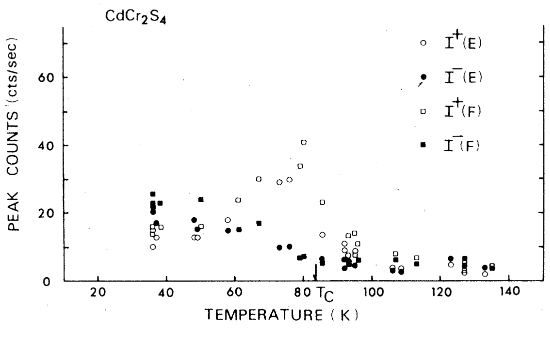

FIG. 4. Temperature dependences of peak counts for phonon lines *E* and *F* with right- and left-circularly polarized incident light.

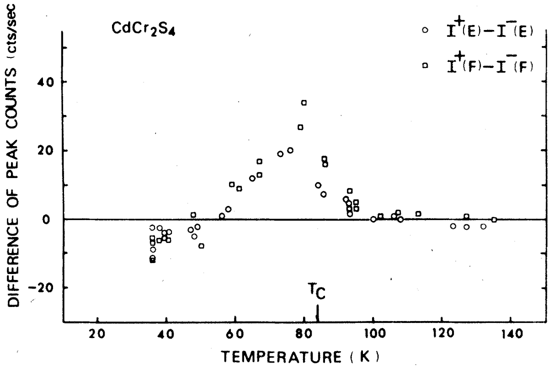

FIG. 5. Temperature dependences of the peak-count differences between right- and left-circularly polarized light for phonon lines *E* and *F*.

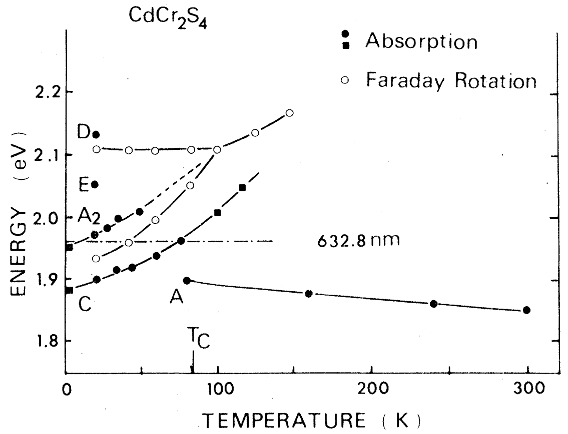

FIG. 6. Temperature dependences of the energies of absorption and Faraday rotation peaks of $CdCr_2S_4$. The absorption peak *A* is due to a crystalline field transition $^4A_2 \rightarrow {}^4T_2$ of Cr^{3+} ions (Ref. 11). The absorption data (solid circle) and Faraday rotation data (open circle) are taken from Ref. 9 and the absorption data (solid square) from Ref. 11.

that the sum of the photon counts for RCP and LCP shows the spin-correlation-type behavior consistent with the previous results.[4] The temperature dependence of the peak counts for RCP has the maximum at a definite temperature; this fact suggests an important role played by resonance effects in the SD phonon scattering. We will give an explanation for the temperature dependence in Sec. IV.

It is interesting here to consider the difference of the temperature dependences in peak counts between RCP and LCP. We note in Fig. 5 that the deviation of the difference from zero occurs a little above T_C where the magnetization starts to increase in the applied field of 2.2 kOe, and also that the sign of the difference changes at about 50 K. If magnetic effects are not considered in the phonon Raman scattering, the peak-count difference should be zero, as mentioned before. Therefore, the deviation of the difference from zero is an indicator of the SD effect on the Raman scattering in magnetic crystals.

IV. ANALYSIS AND DISCUSSION

In order to discuss resonance Raman effects, we need to know the electronic structure of $CdCr_2S_4$ in the region of the excitation energy used. The question of the electronic-level structure near the absorption edge is one of the most intriguing problems in chromium spinels, and the mechanism for the RS transitions is not well understood at present. However, some progress has been made recently in understanding the electronic transitions. The absorption[9,11] and Faraday rotation[9] spectra near the band gap of $CdCr_2S_4$ were reported on thin films at various temperatures. The temperature dependence of several absorption and Faraday rotation peaks are shown in Fig. 6.[9] The notations of the absorption peaks are due to Berger and Ekstrom,[11] and Koshizuka *et al.*[9] These absorption peaks lie on the shoulder of a strong band-to-band absorption at about 2.4 eV. The absorption peak *C* is a well-known RS peak whose energy shifts to the longer-wavelength side with increasing magnetic ordering, as shown in Fig. 6. It was recently pointed out by Koshizuka *et al.* that peak A_2 has the same RS feature as peak *C*.[9] In addition to the red shift of the absorption peaks,[9,11] one finds large magneto-optic effects such as magnetic-circular dichroism,[11] Faraday,[9] and Kerr[19] rotations associated with the RS transitions.

Berger and Ekstrom found, from the magnetic-circular-polarization properties of the absorption spectra, that peaks *C* and A_2 are allowed for right- and left-circularly polarized light, respectively.[11] Therefore, if resonance Raman scattering is measured with circularly polarized light, the polarization properties of resonance scattering should reflect such magnetic-circular dichroism. This was clearly verified in the present experiment; the Raman intensity for the incident light with RCP has the maximum at about 75 K where the energy level *C* coincides with that of the 632.8-nm light as seen in Fig. 6. Thus, we can understand why the intensities of the phonon lines in the configuration (+, −) are much stronger than those in the configuration (−, +) near T_C in Fig. 3. This is due to resonance with level *C*. At low temperatures near 40 K, however, the corresponding two spectra show quite similar patterns. Near 40 K the two levels *C* and A_2 are approximately equidistant from the energy of the exciting line at 632.8 nm. Thus, the two levels contribute an equal amount to the resonance enhancement of the Raman cross section. Therefore, both (+, −) and (−, +) Raman spectra show similar appearances.

The important role of resonance enhancement is thus obvious. Also some effect due to magnetic ordering is definitely related to the SD phonon scattering, because the enhancement depends on the ordering temperature and applied magnetic field.[4,7–10] Magnetic field dependence of the SD phonon scattering was studied by using the circularly polarized light of 647.1 nm in the Faraday configuration.[9] The peak height of lines E and F increases with the magnetization of $CdCr_2S_4$.[9] We postulate the following phenomenological expression for the intensity of SD phonon Raman scattering:

$$I^{\pm} \propto \left| A + \frac{B_{\pm}}{\omega_{\pm}(T) - \omega_i + i\gamma_{\pm}} \left(\frac{M(T)}{M_0} \right) \right|^2 , \qquad (1)$$

where the first term is spin independent and the second term originates in magnetic and resonant effects. The indices + and − on I and B correspond to RCP and LCP of the incident light with photon energy ω_i, respectively. For the incident light of 632.8 nm with RCP, only transition C contributes to the resonance[11]; $\omega_+(T)$ is the energy of transition C, and γ_+ is the damping parameter of this transition. Similarly, only transition A_2 contributes to the resonance with LCP incident light[11]; $\omega_-(T)$ and γ_- are the energy and the damping parameter of transition A_2, respectively. $M(T)/M_0$ is the magnetization ratio of $CdCr_2S_4$ to its zero temperature value, and $B_{\pm}$ is the coupling parameter.

In Fig. 7, the temperature dependences of peak counts of line F are given again for both RCP and LCP of the incident light. Since the thermal change of the linewidth is small, the peak height is linearly proportional to the integrated intensity of the phonon line. The solid and broken curves are calculated from Eq. (1) by using the following parameters: $A=2.2$, $B_+=0.36$, and $\gamma_+=0.035$ eV for $I^+(F)$ and $A=2.2$, $B_-=-1.14$, and $\gamma_-=0.19$ eV for $I^-(F)$.

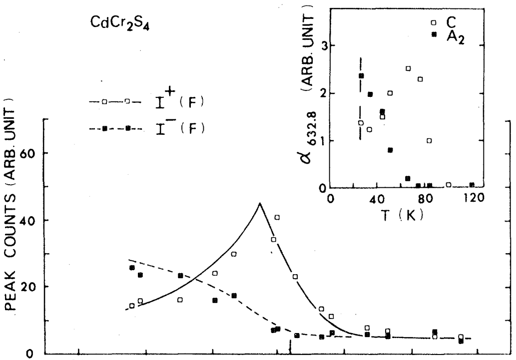

FIG. 7. Experimental and calculated temperature dependences of the peak counts for phonon line F. The inset shows the temperature dependences of the contribution of RS transitions C and A_2 to the absorption coefficient α of $CdCr_2S_4$ at 632.8 nm.

The energy values of $\omega_{\pm}(T)$ are obtained from Fig. 6. To get the ratio $M(T)/M_0$, the temperature-dependence data of the magnetization at 2.0 kOe measured by Yokoyama[20] were adopted. The spin-independent term A is determined from the experimental values in the paramagnetic state, and the coupling parameter $B_{\pm}$ and damping factor $\gamma_{\pm}$ are determined from the low-temperature values below T_C. The calculated temperature dependences are in good agreement with the experimental results. However, it is necessary to consider whether or not these parameters are meaningful. The damping parameter γ is associated with the relaxation rate of the excited states, that is, the width of the corresponding absorption bands. In fact, the width 0.03 eV of the RS absorption band C around T_C[9] is equal to the damping factor γ_+. The agreement is excellent. The width of the absorption band A_2 is not well determined near T_C, but it is definitely wider than that of band C.[9] Therefore, the present result is consistent with the absorption data in that the damping factor γ_- is larger than γ_+. It is interesting to note that the signs of the coupling parameter B are opposite for B_+ and B_-. However, the reason for this sign difference is not obvious.

Next we will consider the resonance enhancement from another point of view. According to Falicov *et al.*[12,13] and Klein,[14] resonance scattering is equivalent to a real transition (absorption) into a resonant state followed by "hot luminescence," provided that interferences with nonresonant amplitudes can be neglected. In the case of a single resonance, the Raman cross section takes a very simple approximate form[13]:

$$d\sigma_{\text{Raman}} = \alpha_{\text{abs}}(a)[\gamma_{\text{tot}}(a)]^{-1} d\sigma_{\text{rad}}(a) \ . \qquad (2)$$

Here $\alpha_{\text{abs}}(a)$ is the contribution to the absorption cross section of the resonant state a; $\gamma_{\text{tot}}(a)$ is the total decay rate of state a, including radiative and nonradiative processes; and $d\sigma_{\text{rad}}(a)$ is the radiative decay rate of state a. The inset in Fig. 7 shows the contributions of resonant transitions C and A_2 to the absorption cross section at 632.8 nm.

The total absorption spectrum in this wavelength region consists of a broad shoulder of a strong band due to a band-to-band transition and relatively weak peaks C, A_2, and others which are superposed on the background of the broad shoulder. In obtaining the estimate of absorption due to the RS absorption bands C and A_2 shown in the inset of Fig. 7, the background was subtracted from the total absorption. The large uncertainty indicated in Fig. 7 for $\alpha(T)_{632.8}$ arises from the fact that the contributions from bands C and A_2 were obtained as a small difference between two large numbers. In the temperature dependence of Raman cross section, the absorption correction could be neglected because the variation of the *total* absorption coefficient in this temperature range is less than ten percent, although the thermal change of the RS absorption bands is large, as shown in Fig. 7. Although one cannot make rigorously quantitative comparisons because of large uncertainties, one can see the general agreement between the temperature dependences of the absorption coefficient at 632.8 nm and the Raman-scattering intensities of RCP and LCP incident light. This means that the anomalous temperature dependence of the Raman intensity is mainly due to the SD effect of the absorption cross section rather than the temperature dependence of the radiative or nonradiative decay processes following the resonant absorption. The magnetic-circular-polarization property of the Raman spectra in Fig. 2 gives clear support for this explanation.

Although various models have been proposed for the SD phenomena, especially for the "red shift" of the absorption edge, there seems to be no conclusive interpretation in chromium chalcogenide spinels. There are roughly two groups of prevailing theories: (i) One is based on the band model of ideal crystals. In this category, there are two complementary ways of explaining the red shift. The Haas picture[21] of the spin-polarized bands is justified in the wide-band scheme of the conduction band, i.e., $IS \ll W$ where I and W are the s-d interaction coefficient and the relevant bandwidth, respectively. This theory cannot be applied to the present system for several reasons; for instance, it predicts the band splitting proportional to the total magnetization. However, experimentally the red shift is found to start above the Curie temperature T_C. In contrast to this theory, the Nagaev approach[2] is useful under the condition $IS \gg W$. According to this theory the red shift is due to broadening of the conduction band with increasing magnetic order. The energy shift is in turn proportional to the spin-correlation function $\langle \vec{S}\cdot\vec{S}_j \rangle$. This prediction approximately agrees with the experimental results. (ii) Another group of theories is based on the presence of imperfections such as sulfer vacancies. Harbeke and Lehmann interpreted the red shift as due to localized states near imperfections affected by the s-d interaction.[22] This idea was based on the sample-dependent behavior and the singlet nature of the final state of the RS transition. This idea was developed by Capek[23] to a simple theoretical model which predicts the red shift governed by the short-range spin-correlation function. As another imperfection model to explain the red shift in $CdCr_2S_4$, Natsume and Kamimura proposed a "magnetic-F-center" model which consists of two electrons trapped at an anion vacancy with their spins parallel at low temperatures.[24]

We will discuss these models on the basis of our Raman-scattering studies. In comparing the intrinsic band model with the imperfection model, the latter seems to be preferable, because we found the breakdown of polarization selection rules for Raman active phonon modes in the cubic spinel structure. Linear-polarization properties of the Raman spectra for $CdCr_2S_4$ are given in Ref. 8, where the breakdown of the selection rule is clearly indicated for the SD phonon lines below T_C. This breakdown is far more prominent under the resonance condition with the RS transition (647.1-nm excitation) than with the direct band-to-band transition (514.5-nm excitation).[8] Furthermore, the circular polarization properties shown in Fig. 2 cannot be explained by taking into account the magnetic group $4/mm'm'$ for the cubic spinel with the magnetization vector parallel to the cubic axis. However, it is possible to explain the polarization properties by lowering the symmetry, for example, to trigonal symmetry supposed in the case of the anion vacancy model.

As mentioned above, two imperfection models are proposed: One is associated with the transitions from the valence band (anion p state) to a singlet excited state of an anion vacancy filled with $4s$ electrons from the neighboring Cr atoms.[22,25] Another magnetic-F-center model is accompanied by a spin-reversal excitation between the molecular-orbital levels composed of one Cd^{2+} and three Cr^{3+} ions in the neighborhood of anion vacancies.[24] We will compare these two models now.

We conclude from the present work that the absorption peaks C and A_2 are due to RS transitions allowed by RCP and LCP light, respectively. The C and A_2 peaks in $CdCr_2S_4$ are analogous to the RS peaks in $CdCr_2Se_4$ (Ref. 26) and $ZnCr_2Se_4$.[24] It is natural to suppose that the red shift of the absorption subbands has a common origin for all chromium chalcogenide spinels. The Harbeke and Lehmann model is suitable for explaining the existence of these two subbands which originate in the spin-orbit splitting of the valence band. Furthermore, the following fact adds support to this model: The SD effects on the phonon scattering cannot be observed for the excitation wavelengths corresponding to the intra-atomic d-d transitions,[7,8] that is, the resonance effect can occur only for electronic transitions between rather delocalized states. This result is consistent with the fact that RS transition energies strongly depend on the kinds of A and X site ions in ACr_2X_4.

On the other hand, the temperature dependence of the Raman intensity in Fig. 7 is similar to that of the associated absorption coefficients. The similarity is expected if the thermal variation of the relaxation factor in Eq. (2) is negligibly small in the measured temperature region. It follows that the intensity of the RS absorption itself should increase with magnetic ordering due to the second term in Eq. (1). According to the "magnetic-F-center" model, the twoelectron state trapped at a vacancy is unstable above T_C.[24] This feature is consistent with the above temperature dependence of the absorption intensity. As we discussed already, some imperfection models are preferable for the mechanism of RS transitions. However, more information is necessary to attain a more comprehensive understanding of the situation.

V. CONCLUSION

We determined the details of the circular-polarization properties of the resonance Raman spectra around the Curie temperature of $CdCr_2S_4$. The temperature dependence of the circular-polarization spectra is interpreted using a newly proposed model which takes into account both the resonance-enhancement and the magnetic ordering effects on the scattering intensity. It is found that the RS transitions C and A_2 take part in the SD resonance Raman effect for right- and left-circularly polarized light, respectively. Several models for the RS transitions are discussed in the light of the present Raman-scattering study. The F-center-like vacancy model appears to be preferable for the RS transitions in chromium spinels. However, further information is necessary to reach a definite conclusion. It will be interesting in this context to determine why only certain phonon modes show the SD phonon Raman scattering. This approach will be useful in determining which model is appropriate for the RS transitions and to elucidate the microscopic mechanisms for the SD scattering in ferromagnetic spinel-type semiconductors.

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