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We clarified the magnetic excitation in $\beta$-type X[Pd(dmit)$_2$]$_2$ (X = cation and dmit = 1,3-dithiole-2-thione-4,5-dithiolate) by Raman spectroscopy. We found a Raman signal that was caused by magnetic excitation in a quantum spin-liquid material, EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ (Et = ethyl and Me = methyl), and an antiferromagnetic long-range ordered material, Me$_4$P[Pd(dmit)$_2$]$_2$. In contrast, we did not find the Raman signal in a nonmagnetic charge-ordered material, Et$_2$Me$_2$Sb[Pd(dmit)$_2$]$_2$. Magnetic excitations in EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ and Me$_4$P[Pd(dmit)$_2$]$_2$ were observed as broad-peak structures centered at approximately 380 cm$^{-1}$ in the Raman scattering spectra, although the degrees of spin frustration of the two compounds were different. We discuss the spectral features of these materials, taking into account the multiple-spin interaction.

1. Introduction

Unraveling the electronic state of the ground state of strongly spin-frustrated systems is a central problem in condensed-matter physics.\textsuperscript{1,2} Recently, two types of organic compound, $\beta$-type X[Pd(dmit)$_2$]$_2$ (X = cation and dmit = 1,3-dithiole-2-thione-4,5-dithiolate) and $\kappa$-(BEDT-TTF)$_2$Y (Y = anion), with a strong spin frustration, were investigated using various experimental methods and theoretical approaches. Among the compounds studied, EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ (Et = ethyl and Me = methyl) and $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ have attracted much attention because they are potential quantum spin-liquid materials.\textsuperscript{3,4}

The excited states of spin-liquid materials have been studied by various experimental methods. In procedures that measure heat capacity and thermal transport,\textsuperscript{5,6} EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ showed a gapless magnetic excitation, while EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ showed an anomaly at 1 K in NMR measurements, which is regarded as evidence of a spin gap.\textsuperscript{7} The results of these experiments lead to different physical scenarios; thus, the low-energy excited states are not yet fully understood.

Magnetic excitation can be investigated by another experimental method: Raman scattering spectroscopy. A two-magnon excitation signal has been observed in $\kappa$-(BEDT-TTF)$_2$Y.\textsuperscript{8} That report showed that two $\kappa$-type BEDT-TTF salts, $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, which have different degrees of spin frustration, have been shown to have two-magnon excitation bands below 700 cm$^{-1}$ in common. The energy positions of the two-magnon Raman structures are different between the two $\kappa$-(BEDT-TTF)$_2$Y compounds, although the two materials have similar exchange constants $J$.\textsuperscript{9,10} The center position of the magnetic excitation band of $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ is lower than that of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. This spectral difference results from the difference in the degrees of spin frustration, i.e., a strong spin frustration leads to a reduction in two-magnon excitation energy. This behavior was reproduced using an anisotropic Heisenberg model calculation.\textsuperscript{8,10}

In this article, we focus on three Pd(dmit)$_2$ salts: EtMe$_3$Sb[Pd(dmit)$_2$]$_2$, Me$_4$P[Pd(dmit)$_2$]$_2$, and Et$_2$Me$_2$Sb-Pd(dmit)$_2$ (hereafter, abbreviated as EtMe$_3$Sb, Me$_4$P, and Et$_2$Me$_2$Sb, respectively). These three salts have an isomorphous crystal structure. In X[Pd(dmit)$_2$]$_2$, magnetic Pd(dmit)$_2$ and nonmagnetic cations are stacked in alternate layers.\textsuperscript{11} Two types of Pd(dmit)$_2$ compounds, layers 1 and 2, which have different stacking directions of the Pd(dmit)$_2$ dimer [Fig. 1(a)], alternate along the c-axis. In the Pd(dmit)$_2$ layer, Pd(dmit)$_2$ molecules are strongly dimerized, with the dimers stacked along the $a - b$ axis and the $a + b$ axis in layers 1 and 2, respectively. The cation X has one positive charge, which results in one Pd(dmit)$_2$ dimer with one negative charge.\textsuperscript{11} In addition, in the Pd(dmit)$_2$ layer, a half-filled electronic system consisting of Mott insulators is formed. The dimers’ spins are frustrated because there is antiferromagnetic interaction on the triangular lattice.

As shown in Fig. 1(a), there are three interdimer transfer energies, $t_0$, $t_1$ ($\approx t_0$), and $t_2$, that are used in first-principles density-functional theory calculations.\textsuperscript{12} These three energies connect the dimers to form an isosceles triangular lattice of the Pd(dmit)$_2$ dimer, in which the degree of spin frustration is characterized by the ratio $t'/t$, where $t' = t_1$ and $t = (t_0 + t_2)/2$.\textsuperscript{11} When $t'/t = 1$, a strong frustration is expected. The energy structure in the electronic system has the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the Pd(dmit)$_2$ monomer. When the Pd(dmit)$_2$ molecules are dimerized strongly, the energy levels of the antibonding HOMO and bonding LUMO are inverted.\textsuperscript{11}

For X[Pd(dmit)$_2$]$_2$, $t'/t$ depends on the cation.\textsuperscript{11} In this study, we deal with three strongly dimerized materials, EtMe$_3$Sb, Me$_4$P, and Et$_2$Me$_2$Sb. In these compounds, $t'/t$ is estimated to be 0.91, 0.62, and 1.01 on the basis of the extended Hückel molecular orbital calculation. The difference in $t'/t$ between compounds leads to different magnetic behaviors. The spins for EtMe$_3$Sb show no long-range order because of the strong spin frustration; hence, it is considered that the quantum spin-liquid state is realized in EtMe$_3$Sb.\textsuperscript{3} The spins for Me$_4$P exhibit an antiferromagnetic long-range order below 39 K.\textsuperscript{13} And Et$_2$Me$_2$Sb shows a nonmagnetic charge-ordered state below 70 K.\textsuperscript{14} The spins for which $t'/t = 0.91$ in EtMe$_3$Sb are more strongly frustrated than those for which $t'/t = 0.62$ in Me$_4$P. The exchange constants
2. Experimental Procedure

We measured the Raman scattering spectra between 150 and 2,000 cm\(^{-1}\) using two excitation lasers of 633 nm (1.96 eV) and 488 nm (2.54 eV) wavelengths. The polarization configuration was (αββ), where α is the polarization of the incident light and β is the polarization of the scattered light. We determined the crystal axes by reflectance spectroscopy. According to Ref. 15, only the reflectivity spectrum of the α-axis polarization shows a peak at approximately \(10 \times 10^3\) cm\(^{-1}\). By measuring the polarization dependence of the reflectivity of each sample, we determined the α-axis of the measured sample. The temperature dependence (4–300 K) of the Raman spectra was measured using a conduction-type cryostat.

3. Results and Discussion

3.1 Excitation wavelength dependence of Raman scattering spectra

We measured the excitation wavelength dependence of the Raman spectra for EtMe\(_3\)Sb at 70 K [Figs. 1(b)–1(e)]. As shown in Figs. 1(b) and 1(c), the Raman scattering spectra of the (bb) polarization at excitation wavelengths of 633 and 488 nm have sharp structures, which are attributed to molecular vibrations, and two broad structures, whose peak positions are located at approximately 400 cm\(^{-1}\) (structure A) and above 2,000 cm\(^{-1}\) (structure B); Fig. 1(f) shows a schematic of these two broad structures. These structures were observed in both Raman spectra [Figs. 1(b) and 1(c)], independent of excitation wavelength. This strongly supports the assignment that structures A and B are due to Raman scattering. Similar structures are observed in the (aa) polarized Raman spectrum at an excitation wavelength of 488 nm [Fig. 1(e)]. On the other hand, the Raman spectrum of the (aa) polarization of the 633 nm excitation [Fig. 1(d)] does not clearly show any structure that corresponds to structure A, but instead has another tail structure between 200 and 700 cm\(^{-1}\) [Fig. 1(d)], which is not observed in the 488 nm excitation. The spectral shape of this tail structure is significantly different from those in Figs. 1(b), 1(c), and 1(e); therefore, we labeled the tail structure C. Thus, the Raman scattering spectrum of EtMe\(_3\)Sb has three broad structures: A, B, and C. Since structure C was observed only in the Raman spectrum of the (aa) polarization of the 633 nm excitation, we suggest two possible origins for structure C: One is a resonant Raman signal. The resonance effect could enhance the intensity for structure C for the (aa) polarization of the 633 nm excitation. The other possible origin is photoluminescence. In Fig. 1(h), we plotted the spectra of the emitted light in (aa) polarization, some parts of which are shown in Figs. 1(d) and 1(e), versus the wavenumber of the emitted light. The shapes of the 633 and 488 nm excitation spectra at approximately 16,000 cm\(^{-1}\) are different, suggesting that structure C is not due to photoluminescence but resonance Raman scattering. Considering that a strong intradimer transition along the α-axis is located at approximately \(10 \times 10^3\) cm\(^{-1}\), the enhancement of structure C for (aa) polarization may be ascribed to the resonance effect due to the intradimer transition.\(^{17,18}\)

![Fig. 1](image-url)

Fig. 1. (a) Illustration of the β-type molecular arrangement in layers 1 and 2 of Pd(dmit)\(_2\) salts. Arrows and italic labels indicate crystallographic axes. Ellipses indicate Pd(dmit)\(_2\) molecules, and two Pd(dmit)\(_2\) molecules in the dashed circles form a Pd(dmit)\(_2\) dimer. (b)–(e) Raman scattering spectra at 70 K for EtMe\(_3\)Sb at excitation wavelengths of 633 [(b) and (d)] and 488 nm [(c) and (e)]. (f) and (g) Schematic views of structures A, B, and C in Raman spectra. (h) (aa) polarized Raman spectra. The horizontal axis denotes the observed wavenumber.
Now, we discuss the origin of the broad Raman structure A, which is located at approximately 400 cm$^{-1}$ in Figs. 1(b), 1(c), and 1(e). One possible origin of this structure is magnetic excitation, similar to the case of $\kappa$-(BEDT-TTF)$_2$Y.8) Another possible origin is an electronic Raman signal due to either the Mott–Hubbard band (interdimer transition), the dimer band (intradimer transition), or a Drude-like component.19) These three possibilities are differentiated by investigating the peak positions and the temperature dependence of the spectral weight in structure A.8)

First, with interdimer transition, the Hubbard band transition energy is described by the effective on-site Coulomb repulsion of a Pd(dmit)$_2$ dimer, $U$, which is 690 meV, on the basis of the ab initio two-dimensional extended Hubbard-type multiband models.20) This value is significantly larger than that obtained from our present Raman measurements, so we can exclude the possibility of the Hubbard band transition being the origin of structure A. Second, the intradimer band transition energies of [Pd(dmit)$_2$]$_2$ are reported to be 330 meV (from the bonding LUMO to the antibonding HOMO) and 1.25 eV (from the bonding LUMO to the antibonding LUMO), as determined by optical conductivity measurement.12,17) In the first-principles calculation based on the density-functional theory, the corresponding transition energies are 411 and 941 meV, respectively.12,21) Thus, the intradimer band transition energies are greater than the observed peak energy of structure A. Therefore, we can rule out intradimer transition as the origin of structure A.

3.2 Temperature dependence of Raman scattering spectra

To clarify the origin of structures A and C, we measured the temperature dependences of the (bb) and (aa) polarized Raman scattering spectra using the 633 nm excitation for EtMe$_3$Sb. In Figs. 2(a)–2(c), the (bb) polarized spectra at 10 and 70 K have broad peak structures, which are structure A’s, centered at approximately 400 cm$^{-1}$, while the spectra at 300 K do not have a peak structure but one that increases with decreasing frequency and increases with increasing temperature. The temperature dependence of the (aa) spectra below 800 cm$^{-1}$ is shown in Fig. 2(d). In these spectra, the structure whose intensity increases with decreasing frequency shows an increase in intensity with increasing temperature. These spectral features and the temperature dependence are similar to those of the structure observed in (bb) polarization at 300 K. The structures observed at 300 K in the (aa) and (bb) polarizations have the same physical origin. These behaviors are consistent with those of the Drude carriers, considering that the number of carriers in an insulator generally increases with increasing temperature.

Comparing the (bb) polarized Raman spectra in Figs. 2(a)–2(c), we note that the intensity of structure A decreases with increasing temperature. To study the origin of structure A, we estimated the spectral weight by fitting the experimental spectra. In Figs. 2(a)–2(c), the Raman spectra below 800 cm$^{-1}$ contain several structures: 15 molecular vibrational modes and broad structures A, B, and C [Figs. 1(f) and 1(g)]. We fitted the vibrational modes using 15 Lorentzian functions and reproduced structures A, B, and C using Lorentzians A, B, and C, respectively. In Figs. 2(a)–2(c), the gray solid lines are the sum of Lorentzians B and C. The gray dashed lines are the sum of Lorentzians A, B, and C. Lorentzian A is equal to the sum of Lorentzians B and C and the gray dashed lines are the fitting results of the sum of Lorentzians A, B, and C. (e) The temperature dependence of the spectral weight of the Lorentzian A in the (bb) polarized Raman spectra.

3.3 Cation dependence of Raman scattering spectra

To investigate the $t'/t$ dependence of the magnetic-excitation band position, we measured the cation dependence of the Raman spectra. Figures 3(a)–3(c) show the (bb) polarized Raman scattering spectra (10 K) of Me$_4$P, EtMe$_3$Sb, and Et$_2$Me$_2$Sb, respectively. As shown in Figs. 3(a) and 3(b), the Raman spectra of Me$_4$P and EtMe$_3$Sb have a broad structure at approximately 400 cm$^{-1}$; however, no broad structure is clearly observed in Fig. 3(c).

To elucidate the structures in the Raman spectra below 700 cm$^{-1}$, we performed a fitting analysis. As with the Raman spectra for EtMe$_3$Sb in Figs. 2(a)–2(c), we fitted the 15 sharp structures assigned to molecular vibrations and broad structures A, B, and C using Lorentzian functions.16) In Figs. 3(a)–3(c), the black solid lines are the experimental results and the gray solid lines are the sum of the molecular vibrational modes and Lorentzians A, B, and C. In Figs. 3(d)–3(f), the black solid lines indicate the spectra in which Lorentzians B and C and the molecular vibrational modes are subtracted from the experimental results, and the gray dashed lines indicate Lorentzian A corresponding to magnetic Raman scattering components. Structure A is
observed for the antiferromagnetic long-range ordered material Me₄P and the spin-liquid material EtMe₃Sb, whose center positions are at approximately 400 cm⁻¹ and whose width is 400 cm⁻¹. This is not observed for the nonmagnetic charge-ordered material Et₃Me₂Sb. Considering that the photoexcitation of two-magnon states is possible only in short-range antiferromagnetically ordered spins, the above experimental results show that structure A results from the two-magnon excitation.

Finally, we focus on the peak positions of the two-magnon Raman structure. From the fitting analysis [Figs. 3(d) and 3(e)], the central energies of the two-magnon excitations for Me₄P and EtMe₃Sb are similar and estimated to be 380 cm⁻¹ at 10 K. However, the t'/t values for these compounds are not the same. Thus, the two-magnon excitation energies for Me₄P and EtMe₃Sb do not directly reflect the degree of spin frustration. Recent investigations of two-magnon Raman scattering for κ-(BEDT-TTF)₂Cu[N(CN)₂]Cl demonstrated that two-magnon excitation appears at different energies, reflecting the different degrees of spin frustration. This behavior was reproduced by the calculation in Ref. 8. In the present study, although EtMe₃Sb and Me₄P have different t'/t values and similar J values, the two-magnon excitation bands in the Raman scattering spectra are observed at similar energies. This behavior for the two X[Pd(dmit)₂] compounds is in contrast to that for κ-(BEDT-TTF)₂Y, which is indicative of the contribution of some factor that determines the two-magnon peak position in addition to the degree of spin frustration and the exchange constant.

3.4 Comparison with the Heisenberg model involving ring-exchange terms

To find out why the t'/t dependences of the two-magnon excitation energies are different for X[Pd(dmit)₂] and κ-(BEDT-TTF)₂Y, we compared the experimental results with the theoretically expected behaviors. Recently, the Heisenberg model calculation has been performed for an anisotropic triangular lattice with the ring-exchange term K using the linear spin wave theory. According to Ref. 23, the magnon excitation energy is determined by t'/t and K/J. Firstly, we consider the t'/t dependence of the magnon excitation energy at a fixed K/J. When K/J is sufficiently large, the magnon excitation energy decreases significantly as t'/t approaches 1 from 0. On the other hand, the magnon excitation energy decreases slightly when K/J is small. Secondly, we consider the K/J dependence of the magnon excitation energy at a fixed t'/t. When t'/t is close to 1, the magnon excitation energy decreases with increasing K/J. On the other hand, when t'/t is close to 0, the magnon excitation energy does not depend on K/J.

To evaluate the effect of K/J on the target materials, we calculated K and J using reported parameters. J and J' are respectively defined as $J = 4t^2/U$ and $J' = 4t^2/U$ using the Heisenberg model on the anisotropic triangular lattice. In addition, on the anisotropic triangular lattice, K is defined as $80t^2/U^2$ for the lowest-order approximation. The above relations give $K/J = 20t^2/U^2$. The effective on-site Coulomb repulsion of a dimer, U, and the interdimer transfer energies t and t' are listed in Table I. The Coulomb repulsions U for EtMe₃Sb and κ-(BEDT-TTF)₂Cu[N(CN)₂]Cl were calculated using ab initio two-dimensional extended Hubbard-type multiband models. For X[Pd(dmit)₂] and κ-(BEDT-TTF)₂Y, the Coulomb repulsion U weakly depends on the types of cation and anion, respectively. Therefore, in each group of Pd(dmit)₂ and BEDT-TTF salts, we use the single value of U. The transfer energies t and t', which were calculated by the first-principles density-functional theory calculations, were cited from Refs. 12 and 27.

Using the above equations and values, we showed the values of t'/t and K/J for the target materials in Table I. We compared the values of t'/t and K/J between Me₄P and EtMe₃Sb. The t'/t for Me₄P is smaller than that for EtMe₃Sb and the K/J for Me₄P is larger than that for EtMe₃Sb. Here, we consider the dependence of the magnon excitation energy on the t'/t and K/J. For Me₄P and EtMe₃Sb, changes in the magnon excitation energy resulting from the changes in t'/t and from that in K/J have opposite signs. As a result, we expect that the changes cancel out and that the magnon excitation energies for Me₄P and EtMe₃Sb are similar. Actually, the two-magnon excitation bands for X[Pd(dmit)₂] appear at similar energies. These behaviors are consistent with those expected in theory while taking the ring-exchange term into consideration.

Here, we consider why the two-magnon bands for κ-(BEDT-TTF)₂Y appear at different energies in our previous report. The relations of t'/t and K/J for κ-(BEDT-TTF)₂Cu[N(CN)₂]Cl and κ-(BEDT-TTF)₂Cu₂(NCN)₃ are sim-
ilar to those in the cases of Me 4P and EtMe 3Sb. In comparison with that for \(\kappa\)-(BEDT-TTF)\(_2\)Cu\([\text{N(CN)}_2]\)Cl, the \(t'/t\) ratio for \(\kappa\)-(BEDT-TTF)\(_2\)Cu\([\text{N(CN)}_2]\)Cl is small and its \(K/J\) is large. For \(\kappa\)-(BEDT-TTF)\(_2\)Cu\([\text{N(CN)}_2]\)Cl, \(t'/t\) is sufficiently small. In such a small \(t'/t\) region, the change in the magnon energy with the increase in \(K/J\) is not so large in comparison with that in the case of X[Pd(dmit)\(_2\)]\(_2\) where \(t'/t\) is not so small. As a result, the decrease in magnon energy with the increase in \(K/J\) does not cancel the increase in the magnon energy with the decrease in \(t'/t\). This is in contrast to the case of X[Pd(dmit)\(_2\)]\(_2\).

Thus, our theoretical consideration suggests that the magnon excitation energies for \(\kappa\)-(BEDT-TTF)\(_2\)Cu\([\text{N(CN)}_2]\)Cl and \(\kappa\)-(BEDT-TTF)\(_2\)Cu\([\text{N(CN)}_2]\)CN are different. Moreover, it clearly explains the experimental observation that, in Raman scattering spectra, the two-magnon bands for \(\kappa\)-(BEDT-TTF)\(_2\)Cu\([\text{N(CN)}_2]\)Cl and \(\kappa\)-(BEDT-TTF)\(_2\)Cu\([\text{N(CN)}_2]\)CN appear at different energies.

In this manner, the difference in behavior between the two-magnon bands for X[Pd(dmit)\(_2\)]\(_2\) and \(\kappa\)-(BEDT-TTF)\(_2\)Y is explained by the theory that considers the ring-exchange term. Thus, we experimentally showed that the magnon excitation in X[Pd(dmit)\(_2\)]\(_2\) reflects the multiple-spin interaction more significantly than that in \(\kappa\)-(BEDT-TTF)\(_2\)Y.

4. Conclusions

In summary, we showed the existence of magnetic excitation Raman scattering for \(\beta\)-type X[Pd(dmit)\(_2\)]\(_2\). Magnetic excitation bands were observed for the quantum spin-liquid material EtMe\(_2\)Sb and the antiferromagnetic long-range ordered material Me\(_2\)P. We assigned these magnetic excitation bands to the two-magnon excitation. The two-magnon excitation energies are similar despite the different degrees of spin frustration. We found that the two-magnon excitation energies depend not only on neighbor-spin interaction but also on multiple-spin interaction such as ring exchange interaction, and that such multiple-spin interaction plays an important role in \(\beta\)-type X[Pd(dmit)\(_2\)]\(_2\).

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18) The (ab) and (ba) polarized Raman spectra at an excitation wavelength of 633 nm (not shown) have structure C. Considering that the intensity of structure C in (aa) polarization is larger than that of structure A in (bb) polarization, structure A, if any, might be buried under structure C.
21) H. Seo and T. Tsumuraya, private communication.
25) In our previous report,\(^8\) we adopted a more precise formula for the exchange constants \(J\) and \(J'\): \(J = 4t^2U - 4(6t^4 + t^4 + t^4)/U^3\) and \(J' = 4t^2U - 4(4t^4 + 4t^4 + t^4)/U^3\). These precise equations would not change the magnitude relation between the \(K/J\) values for X[Pd(dmit)\(_2\)]\(_2\) and those for \(\kappa\)-(BEDT-TTF)\(_2\)Y.