V. MAGNETIC EXCITATIONS.

RAMAN SCATTERING STUDIES OF SPIN ORDER AND FLUCTUATIONS IN THE EUROPIUM CHALCOGENIDES

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Résumé.— Ici on examine la diffusion de lumière, à la fois inélastique et dépendante de la phase magnétique, des phonons dans les chalcogénides d'euporium attirant l'attention sur l'allure des spectres près des transitions à phase magnétique. Par suite du mécanisme de diffusion Raman "un phonon-un spin" qui donne lieu à ces spectres, on observe des lignes Raman du premier ordre de type aussi large ($\Delta\nu \sim 30 \text{ cm}^{-1}$) que fin ($\Delta\nu \leq 1 \text{ cm}^{-1}$). La dépendance de température calculée des spectres Raman à lignes larges s'est rapportée aux variations de spin et est comparée avec l'expérience. On montre que les lignes fines, observées dans les phases magnétiques ordonnées aux énergies de phonon non $\vec{q} = 0$, sont une mesure directe du carré du paramètre d'ordre (exposant β). Les spectres Raman observés sont mis en corrélation avec les propriétés magnétiques des composés EuSe et EuTe près des transitions à phase métamagnétique (EuSe) et spin flop-paramagnétique (EuTe). La théorie aussi bien que l'expérience montrent que la dépendance de température et de champ magnétique de ces spectres Raman est une sonde sensible des variations de spin et de l'ordre de spin dans ces substances.

Abstract.— Magnetic phase dependent, inelastic light scattering from phonons in the europium chalcogenides is reviewed with an emphasis on the behavior of the spectra near magnetic phase transitions. As a result of the one phonon-one spin Raman scattering mechanism which gives rise to these spectra, both broad ($\Delta\nu \sim 30 \text{ cm}^{-1}$) and sharp ($\Delta\nu \leq 1 \text{ cm}^{-1}$) first-order Raman lines are observed. The calculated temperature dependence of the broadline Raman spectra is related to spin fluctuations and compared with experiment. The sharp lines, observed in the ordered magnetic phases at non $\vec{q} = 0$ phonon energies, are shown to be a direct measure of the square of the order parameter (exponent β). The observed Raman spectra are correlated with the magnetic properties of EuSe and EuTe near the metamagnetic (EuSe) and spin flop to paramagnetic (EuTe) phase transitions. Both theory and experiment indicate that the temperature and magnetic field dependence of these Raman spectra is a sensitive probe of spin fluctuations and spin order in these materials.

1. **Introduction.**— The europium chalcogenides (EuO, EuS, EuSe and EuTe) are a family of magnetic semiconductors in which the electronic, optical, and magnetic properties are interrelated /1/. Recent Raman scattering experiments on these materials show that their phonon spectra, which are forbidden in first-order, are magnetic phase dependent /2-13/. Although the europium chalcogenides exhibit a wide variety of magnetic phases / 13 - 15 / (EuO and EuS are ferromagnets ; EuSe is a metamagnet with one- two- three- and four- sublattice phases ; EuTe is a two-sublattice antiferromagnet), the general features of their Raman spectra are the same. In the paramagnetic phase, a broad spectral line has

been observed with a full width /2-10,12,13/ $\Delta\nu \sim 30 \text{ cm}^{-1}$ spanning the entire LO phonon branch. As magnetic ordering occurs, this "broadline" due to spin-disorder scattering is quenched, and sharp lines ($\Delta\nu < 0.6 \text{ cm}^{-1}$) are observed /2,3,5,7-13/.

In this review, we focus on the temperature and magnetic field dependence of the one-phonon Raman spectra /8,11,14,15/⁽¹⁾. We show theoretically and cite experimental evidence that although a single, one phonon-one spin excitation mechanism accounts for both the broad and sharp lines, the broadlines are sensitive to spin fluctuations while the sharp line spectra measure the magnetic order parameter. Detailed theoretical studies of the dependence of the Raman

⁺ Research done at Francis Bitter Lab (supported by NSF) and Physics Department, Massachusetts Institute of Technology.

(1) (For discussions of the harmonic and two-phonon spectra see Refs.3,6,7.)

cross section on the electronic (e.g. resonance effects) and lattice (e.g. phonon dispersion) properties of the europium chalcogenides have been presented in refs. /16/ and /17/.

Section 2 summarizes the one phonon-one spin Raman excitation mechanism and the general expression for the light scattering intensity in terms of two-spin correlation functions. In Section 3, we relate the broadline spectra observed in the paramagnetic phase to spin fluctuations. The temperature dependence of the broad line integrated intensity, $I(T)$, near magnetic phase transitions is calculated and related to the specific heat. Different behavior for $I(T)$ is predicted for ferromagnets (EuO, EuS) and antiferromagnets (EuTe) and the results for EuS are compared with experiment /6,18/. The evolution of the observed /3/ Raman spectrum in EuSe from a single to a double peaked structure as T approaches the critical temperature from above $T \rightarrow T_C^+$, is correlated with the spin fluctuations associated with the paramagnetic to four-sublattice antiferromagnetic transition. Section 4 shows how the intensity of the sharp lines observed in the ordered magnetic phases of EuSe and EuTe can be used to directly measure the magnetic order parameter. The phonon mode assignments of the observed Raman lines in EuSe are correlated with the predicted selection rules to show that the one phonon-one spin scattering mechanism predominates. In Section 5 we conclude with some suggestions for future work.

2. Raman Cross Section.— The Raman scattering mechanism which has recently been established /4,14,16,17,19/ for first-order scattering in the europium chalcogenides involves a virtual process in which an incident photon of energy $\hbar\omega_i$ excites the electronic system from the $4f^7$ ground state to the $4f^65d$ excited state. The excited electrons and holes interact with both the phonons and the spins through the large (~ 0.6 eV) spin-orbit coupling in this excited electronic state. Finally, the

electrons return to their ground state, emitting a photon of energy $\hbar\omega_s$. The Raman cross section is calculated /4,14,16,17,19/ using fourth order perturbation theory including the interactions between (1) the electrons (holes) and the incident photon (2) the electrons (holes) and the scattered photon (3) spin and orbital motions of electrons and holes (4) the electrons (holes) and phonons. In the dipole approximation, the Raman intensity for this one phonon-one spin process is proportional to $\underline{S}(\omega)$, where

$$\underline{S}(\omega) = \underline{S}_B(\omega) + \underline{S}_S(\omega) \quad (1a)$$

$$\underline{S}_B(\omega) = \sum_{\vec{q}, \sigma, \sigma'} f_{isj\sigma\sigma'}(\vec{q}) \langle \tilde{S}_\sigma(-\vec{q}) \tilde{S}_{\sigma'}(\vec{q}, \omega - \omega_j(\vec{q})) \rangle \quad (1b)$$

$$\underline{S}_S(\omega) = \sum_{\vec{q}, \sigma, \sigma'} f_{isj\sigma\sigma'}(\vec{q}_0) N_\sigma N_{\sigma'} \delta(\omega - \omega_j(\vec{q}_0)) \quad (1c)$$

In eq. (1), $\underline{S}_B(\omega)$ and $\underline{S}_S(\omega)$ refer to the broad line (spin-disorder) and sharp line (spin-order) spectra respectively. Here we consider Stokes scattering and neglect the phonon Bose factor which is very weakly temperature dependent in the temperature range of interest (see table I). The photon energy loss is $\hbar\omega = \hbar(\omega_i - \omega_s)$ while $f_{isj\sigma\sigma'}(\vec{q})$ is a form factor given by

$$f_{isj\sigma\sigma'}(\vec{q}) = \chi_{isj\sigma}(\vec{q}) \chi_{isj\sigma'}^*(\vec{q}) \quad (1d)$$

where $\chi_{isj\sigma}(\vec{q})$ is the wavevector-dependent Raman tensor which consists of the electronic matrix elements corresponding to the electron-photon, -phonon, and -spin interactions. The indices i and s refer to the incident and scattered photons with polarization vectors $\vec{e}_i$ and $\vec{e}_s$, respectively, j refers to the phonon branch, and σ, σ' label the x, y, z components of the Fourier transform of the spin operators $S_\sigma(\vec{q})$. Since we shall focus on the relationship between $\underline{S}(\omega)$ and the spin correlation functions, we shall treat the form factor as a phenomenological tensor whose dependence on i, s, σ and $\vec{q}$ can be determined from symmetry arguments /14/. In addition, we assume that $\hbar\omega_i$ and $\hbar\omega_s$ are not close to an electronic resonance so perturbation theory is valid and $f_{isj\sigma\sigma'}(\vec{q})$ is spin-independent.

Table I.- Spin order and Raman active sharp lines for optical phonons in europium chalcogenides (one phonon-one spin mechanism).

Material	Magnetic order	Optic phonons	Observed frequencies
EuO	Ferromagnet $T_c = 69.3$ K	$\omega_{LO}^*(o)$	-
		$\omega_{TO}^*(o)$	-
EuS	Ferromagnet $T_c = 16.6$ K	$\omega_{LO}^*(o)$	a) 278 cm^{-1}
		$\omega_{TO}^*(o)$	-
EuSe	Four-sublattice $T_N = 4.6$ K	$\omega_{LO}^+(\vec{q}_L/2)$	a,b) 176 cm^{-1}
		$\omega_{TO}^+(\vec{q}_L/2)$	a,b) 130 cm^{-1}
	Three-sublattice $T_N = 2.8$ K	$\omega_{LO}(2\vec{q}_L/3)$	a,b) 169 cm^{-1}
		$\omega_{TO}(2\vec{q}_L/3)$	-
	Two-sublattice $T_N = 1.8$ K	$\omega_{LO}^+(\vec{q}_L)$	a,b) 153 cm^{-1}
		$\omega_{TO}^+(\vec{q}_L)$	-
EuTe	Two-sublattice $T_N = 9.6$ K	$\omega_{LO}^+(\vec{q}_L)$	c,d) 113 cm^{-1}
		$\omega_{TO}^+(\vec{q}_L)$	-

* Forbidden in dipole approximation. Allowed only in resonant, wavevector dependent Raman scattering.

† Allowed only in one spin scattering - forbidden for two spin mechanism, ($\vec{q}_L = \frac{\pi}{a} (1,1,1)$)

a) Ref./3/ c) Ref./7/
b) Ref./11/ d) Ref.10/

Furthermore, we only consider LO phonon scattering ($j=LO$), since both theory /4,16, 17/ and experiment /4,20/ indicate that this scattering channel is dominant. For a detailed treatment of the Raman spectra in terms of the electronic matrix elements and resonance effects, see refs./4,14,16,17,21/.

The term $\underline{S}_B(\omega)$ in eq. (1a) arises from spin fluctuations $\tilde{S}_0 = S_0 - \langle S_0 \rangle$ and is proportional to the two-spin correlation function. The term $\underline{S}_S(\omega)$ of eq.(1a) is proportional to the square of the staggered magnetization $N_0 = \langle S_0(\vec{q}_0) \rangle$, and gives rise to a sharp line at the phonon energy corresponding to the wavevector $\vec{q}_0$ where $\langle \tilde{S}(\vec{q}_0) \rangle$ is nonzero in the ordered magnetic phase. One can thus think of these sharp lines as "Bragg" scattering of the phonons by the ordered magnetic superlattice /14,19/. The factorization of the correlation function, originally involving two-spin and two-

phonon operators into the product of a two-spin correlation function and a phonon Bose factor, is justified for Raman scattering from optical phonons. The direct interaction between spins and optical phonons is small since there is no spin-orbit coupling in the $4f^7$ ground state and any spin-phonon interaction arises from a phonon modulation of the exchange energy ($\sim 10 \text{ cm}^{-1}$ compared to $\omega_{LO} \sim 200 \text{ cm}^{-1}$). In addition, the observed /22/ magnetostriction is extremely small with the change in lattice constant given by $\Delta a/a \sim 5 \times 10^{-5}$. Thus, the phonons are only coupled to the spins via the virtually excited electrons, with little effect on the intrinsic properties of either the phonons or spins, since the Raman process is weak.

Within the context of the perturbation theory discussed here, one can show /11,14, 16,17/ that the Raman tensor $\chi_{isj\sigma}(\vec{q})$ is

antisymmetric under the exchange of the incident and scattered polarizations. The antisymmetric nature of the Raman tensor which arises from the antisymmetry of the spin operators under time reversal, has been demonstrated experimentally by Merlin et al /4,12/ who show that the antisymmetric ($e_i^x e_s^y - e_i^y e_s^x$) components of the Raman tensor dominate the observed spectra. If one further assumes /4,16,17/ that the electrons and holes couple only to the fully symmetric (Γ_1^+) displacements of the non-magnetic ions one finds that for $j = \text{LO}$

$$f_{isj\sigma\sigma'}(\vec{q}) = \delta_{\sigma,z} \delta_{\sigma'\sigma} [\delta_{i,x} \delta_{s,y} - \delta_{i,y} \delta_{s,x}] g(\vec{q}) \quad (2a)$$

$$g(\vec{q}) = g_0 [\sin^2 q_x a / 2 + \sin^2 q_y a / 2 + \sin^2 q_z a / 2] \quad (2b)$$

where g_0 is a constant. A more general symmetry analysis /11,14,16/ confirms the essential features of eq. (2) with the Raman tensor tending to zero as $\vec{q}$ goes to zero, and to a maximum as $\vec{q}$ approaches $\vec{q}_L = \pi/a(1,1,1)$ where a is the cubic lattice constant. The $\vec{q}$ dependence of the form factor plays an important role in determining the Raman lineshapes and intensities, as shown below.

3. Spin fluctuations : broad lines.- 3.1.

Raman lineshapes.- In the paramagnetic phase, the order parameter (staggered magnetization) N_0 is identically zero, and the spectrum consists of spin disorder scattering as described by eq. (1b). At high temperatures, ($T \gg T_c$) the spins are uncorrelated so that the two-spin correlation function is $\vec{q}$ -independent, and the Raman lineshape for all four europium chalcogenides reflects the LO-phonon density of states weighted by the wavevector-dependent form factor /4,3,12,17,19/. Since the form factor has a maximum at $\vec{q}_L$ the spectrum consists of a broad line peaked at $\omega_{\text{LO}}(\vec{q}_L)$ as shown for EuS in figure 1. However, near magnetic phase transitions ($T \sim T_c$), large fluctuations of the spins occur near $\vec{q} = \vec{q}_0$, where $\vec{q}_0$ describes the low temperature ordered magnetic state (see Table I). For ferromagnets (EuO, EuS) the vanishing of the Raman tensor at $\vec{q}_0 = 0$ results in no dramatic changes in

the broadline lineshape for $T > T_c$. However, for $T \ll T_c$ large shifts of the broadline peak to higher phonon energies are observed /6,7,12/. These shifts have been interpreted /7,12/ as arising from one phonon-one magnon scattering which weighs heavily the contributions near $\vec{q} = 0$, resulting in a phonon spectrum upshifted in energy from $\omega_{\text{LO}}(\vec{q}_L)$. On the other hand, spin fluctuation effects are observed /3,8,9/ in EuSe even for $T > T_c$ for the paramagnetic to four sublattice transition at 4.6 K at which a shift is expected in the peak of the broadline from $\vec{q}_L$ to $\vec{q}_0 = \vec{q}_L/2$ where the Raman is non zero.

Fig. 1.- Polarized Raman spectrum of EuS.

(after ref./4/)

We have calculated the Raman line shape for the broad line in EuSe for both $T \gg T_c$ and $T \sim T_c$ using both the quasi elastic and mean field approximations for the two-spin correlation function /23/ :

$$\langle \tilde{S}_\sigma(\vec{q}, 0) \tilde{S}_\sigma(-\vec{q}, \omega) \rangle = \frac{T/T_c}{\epsilon + \Delta J(\vec{q})} \frac{1}{3} S(S+1) \delta(\omega) \quad (3a)$$

$$\Delta J(\vec{q}) = [J(\vec{q}_0) - J(\vec{q})] / J(\vec{q}_0) \quad (3b)$$

$$J(\vec{q}) = \sum_{\vec{R}} e^{i\vec{q} \cdot \vec{R}} J(\vec{R}). \quad (3c)$$

where $t = (T - T_c)/T_c$. In eq. (3c) the sum over $\vec{R}$ runs over the nearest and next nearest neighbors with exchange constants $J_1 = .167$ K and $J_2 = -.158$ K respectively. The form factor was approximated as in eq. (2) and the phonon dispersion curves for the LO branch were assumed to obey the "tight binding" form,

$$\omega_{LO}^2(\vec{q}) = \omega_{LO}^2(\vec{q}_L) + \frac{1}{3} [\omega_{LO}^2(0) - \omega_{LO}^2(\vec{q}_L)] p(\vec{q}) \quad (4a)$$

$$p(\vec{q}) = \frac{1}{2} \sum_{i \neq j} \cos q_i a / 2 \cos q_j a / 2 \quad (4b)$$

where $\omega_{LO}(0) = 182 \text{ cm}^{-1}$ and $\omega_{LO}(\vec{q}_L) = 153 \text{ cm}^{-1}$ as given by experiment /3,5,7,13/.

The results of these calculations are shown in figure 2 where the Raman intensity is plotted as a function of ω .

Fig. 2.- Raman broad line intensity (arbitrary units) vs. ω (Raman shift in cm^{-1}) for EuSe, calculated using eq. (3). The calculated curves are for room temperature (paramagnetic phase) and for $T = T_c = 4.6 \text{ K}$. The peak at 167 cm^{-1} is due to spin fluctuations of wave vector $\vec{q}_L/2$. The inset shows the pertinent experimental results, displaced vertically for clarity (see ref. /3/).

At high temperatures, the line shape resembles that of EuS (Fig.1) with a peak at $\omega_{LO}(\vec{q}_L)$ and a width comparable to the dispersion of the LO branch. However, at T_c the spin fluctuations with wavevectors near $\vec{q}_0$ increase, giving rise to a new peak in the spectrum at $\omega_{LO}(\vec{q}_L/2)$. The intensity of the peak at $\omega_{LO}(\vec{q}_L)$ also increases since

there are large fluctuations near $\vec{q}_L$ (associated with the two-sublattice phase, almost degenerate in energy with the four-sublattice phase). Although both Raman /15/ and Mössbauer /25/ data indicate that the transition at 4.6 K is first-order, we note the qualitative agreement between theory (which assumed a second-order transition) and experiment as shown in figure 2. The development of the spectrum from a single peak at $\omega_{LO}(\vec{q}_L)$ for $T \gg T_c$ to a double peaked structure for $T \approx T_c$ indicates the sensitivity of the broadline spectrum to the large (but not critical) fluctuations at the spin-ordering wavevector $\vec{q}_L/2$.

3.2. Integrated intensity.- Although one can extract qualitative information about the spin system from the Raman broadline lineshape, the behavior of the temperature dependence of the magnetic order and fluctuations can best be studied by measuring the integrated Raman intensity. For zero external magnetic field ($H = 0$), the broadline integrated intensity $I(T)$ is given by

$$I(T) = \sum_{\vec{q}, \sigma, \sigma'} \sum_{J=L,0} f_{jsj\sigma\sigma'}(\vec{q}) G_{\sigma\sigma'}(\vec{q}) \quad (5a)$$

where $G_{\sigma\sigma'}(\vec{q})$ is the temperature dependent, static, two-spin correlation function

$$G_{\sigma\sigma'}(\vec{q}) = \frac{\langle \tilde{S}_\sigma(\vec{q}) \tilde{S}_{\sigma'}(-\vec{q}) \rangle}{S(S+1)} \quad (5b)$$

Near second-order phase transitions at critical temperature T_c $G_{\sigma\sigma'}(\vec{q})$ has a maximum at $\vec{q} = \vec{q}_0$ due to the large spin fluctuations near T_c .

For $T > T_c$ the broadline integrated intensity can be related to the specific heat C_H which for $T > T_c$ has the form /26,27/

$$C_H = \frac{\partial}{\partial T} \left[- \sum_{\vec{q}} J(\vec{q}) G_{\sigma\sigma'}(\vec{q}) \right] \sim B + A t^{-\alpha} \quad (6)$$

where $J(\vec{q})$ is defined in eq.(3c) and A and B are constants. Recent renormalization group calculations have shown that near second-order phase transitions the critical exponents /26,27/ are functions of the spatial dimensionality (d) and spin dimensionality (n). For three dimensional ($d=3$) Heisenberg ($n=3$) or XY ($n=2$) systems, B is

positive while α and A are negative/27/. In EuO, the ratio B/A has been measured /28,29/ to be -0.91. By expanding both the form factor and $J(\vec{q})$ near $\vec{q} = 0$ for a ferromagnet and near $\vec{q} = \vec{q}_L$ for an antiferromagnet, one can show /11,14,16/ that a comparison of eq.(6) with eqs.(2) and (5) indicates that

$$I(T) - I(T_c) = C [Bt + At^{1-\alpha}] \quad (7)$$

In eq.(7) the proportionality constant C is positive for ferromagnets and negative for antiferromagnets. The integrated scattering intensity $I(T)$ has a cusp at T_c for the antiferromagnet and decreases as $T \rightarrow T_c^+$ for the ferromagnet, because of the different $\vec{q}$ dependence of the form factors near the wavevectors at which the correlation functions are large.

The temperature dependence of $I(T)$ can also be calculated directly from the mean field, Ornstein-Zernike (OZ) form for the correlation function /30,31/.

$$G_{\sigma\sigma} \sim (\kappa^2 + q^2)^{-1} \quad (8)$$

where κ is the inverse correlation length and is proportional to $t^{1/2}$. The OZ form for the correlation function can be derived from a simple Landau expansion /27/ and provides a good description of mean field fluctuations near $\vec{q} = \vec{q}_0$. However, in order to describe the large wavevector ($q > \kappa$) fluctuations, studies /31/ of the temperature dependence of the electrical resistivity in magnetic systems near second-order phase transitions have suggested that a normalized Ornstein-Zernike (NOZ) form for the correlation function be used. The normalization factor, which depends only on the temperature through κ , is determined by requiring the correlation function of eq.(8) to satisfy the sum rule $\sum_{\vec{q}} G_{\sigma\sigma}(\vec{q}) = 1$.

Figure 3 shows $I(T)/I(\infty)$ for ferromagnetic EuS calculated /14/ using both the normalized and unnormalized forms of the correlation functions for $T > T_c$. For $T < T_c$, the RPA forms for $G_{\sigma\sigma}(\vec{q})$ have been used. The NOZ theory predicts a decrease in $I(T)$

near T_c because the large wave vector contributions are weighted most heavily in the Raman tensor(eq.(2)) and because the correlation function decreases near T_c for large $\vec{q}$ in the ferromagnet.

Fig. 3.- Calculated broad line integrated intensity vs. reduced temperature (T/T_c) for EuS. The intensity, $I(T)$, is normalized to $I(\infty)$. The data points, taken from the peak intensity of the Raman spectra, are from Tekippe et al. (Ref./18/) [open circles], and Schlegel and Wachter (Ref./6/) [open squares]. The point (.) at $T = 0$ is the calculated, spin-wave result of Safran et al. (Refs./14/ /19/).

This is in contrast to the OZ form of the correlation function which predicts a maximum at T_c for all $\vec{q}$ values. The data points for the broad line peak intensity are taken from ref./6/ and /18/. The good agreement between both sets of data and the NOZ theory, which predicts a decrease in $I(T)$ as T approaches T_c from above ($T \rightarrow T_c^+$), is evidence of the importance of the large $\vec{q}$ fluctuations in the Raman process. Near $T=0$, the data of ref./6/ is in good agreement with the value of $I(0)/I(\infty) = 2/9$ as predicted from spin wave theory. The smaller value of this ratio obtained the measurements of ref./18/ is possibly a result of the comparison of the theoretical integrated intensities with the measured peak intensities. However, both sets of data indicate that $I(0) \neq 0$ consistent with the low temperature behavior of $S_B(\omega)$ which describes the creation of one phonon and

one magnon even at $T=0$ /14,16,17,19/.

For a two-sublattice antiferromagnet near a second-order phase transition with $\vec{q}_0 = \vec{q}_L$, calculations of $I(T)$ indicate that there is a maximum at T_N and a square root singularity in $dI(T)/dT$ at T_N in both the OZ and NOZ theories. This is because the scattering in the antiferromagnet is composed mainly of fluctuations with wavevectors near $\vec{q}_L$ where the form factor is a maximum and where the correlation function diverges in both the OZ and NOZ theories. This is in contrast to the behavior of $I(T)$ near T_c for the ferromagnet where the large fluctuations at $\vec{q}=0$ are suppressed in the spectrum due to the vanishing of the Raman tensor at this wavevector.

Thus, the broadline Raman spectrum of the europium chalcogenides is sensitive to the fluctuations of the spins for $T \sim T_c$. In the next Section, we show that the long range magnetic order which develops for $T < T_c$ results in a sharp line Raman spectrum whose integrated intensity directly measures the square of the magnetic order parameter.

4. Spin order : sharp lines.— Below the magnetic phase transition, the broad line due to spin disorder scattering is quenched and sharp lines are observed /3/. In EuTe a sharp line has been reported in the two-sublattice phase at $\omega_{LO}(\vec{q}_L) = 113 \text{ cm}^{-1}$ /7,10/. In EuSe, sharp lines corresponding to $\omega_{LO}(\vec{q}_L/2)$ (four-sublattice = AF-I), $\omega_{LO}(2\vec{q}_L/3)$ (three-sublattice = Ferri), and $\omega_{LO}(\vec{q}_L)$ (two-sublattice = AF-II), have been observed as shown in figure 4. The assignments of these lines are in agreement with the predictions of the one phonon-one spin mechanism (see Table I). In contrast to the linear spin Raman mechanism, a Raman process quadratic /9,13,16,32/ in the spin would give rise to a sharp line at $\omega_{LO}(\vec{q}_L)$ in the four-sublattice phase and a sharp line at $\omega_{LO}(\vec{q} = 0)$ in the two-sublattice phase. These lines have not been observed, indicating the dominance of the one spin mechanism. However, several resonance Raman lines observed in both EuSe /9,13/ and EuTe /7,10,

12/ have been attributed to a one phonon-two spin scattering mechanism which may become significant when $\hbar\omega_i$ is near an electronic resonance for the $4f^7$ to $4f^65d$ transition and our perturbation theory breaks down.

Fig. 4.— Observed zero-field Raman spectra in EuSe for right angle scattering. The Raman frequencies are indicated for the four sublattice antiferromagnetic phase (4.2 K), the three sublattice ferrimagnetic phase (2 K), and the two sublattice antiferromagnetic phase (1.7 K). These frequencies correspond to $\omega_{LO}(\vec{q}_L/2)$, $\omega_{LO}(2\vec{q}_L/3)$ and $\omega_{LO}(\vec{q}_L)$ respectively, in agreement with the one-phonon-one-spin mechanism (see Table I). The magnetic phase diagram of EuSe is shown in the inset /22/. For a discussion of the experimental details see refs./3/,/13/.

Eq.(1c) indicates that the intensities of the one phonon- one spin sharp lines are proportional to the square of the staggered magnetization. Thus, the sharp line intensity can be used to measure directly the temperature and magnetic field dependence of the order parameter which varies as $N \sim (T_c - T)^\beta$ near second-order phase transitions and is discontinuous at T_c for first-order transitions.

In support of this latter prediction, figure 5 shows the Raman spectrum of EuSe for $H=0$ and $\hbar\omega_i=1.83 \text{ eV}$ using the apparatus described in ref./3/. Results are shown for

temperatures above and below the ferrimagnetic to antiferromagnetic transition at $T=1.8$ K (see Table I).

Fig. 5.- Temperature dependence of the Raman scattering in EuSe for $H = 0$ and T near the magnetic phase transition at 1.8 K. The temperatures have been shifted upward by 0.15 K to account for the average laser heating of the scattering volume. (a) Raman spectra above and below the critical temperature $T_C = 1.8$ K, corresponding to the three-sublattice phase ($\uparrow\uparrow\uparrow$) and the two-sublattice phase ($\uparrow\uparrow$) respectively. (b) Temperature dependence of the peak Raman intensities for the two- and three-sublattice phases, where the data points are from experiments and the dashed lines represent the step function temperature dependence expected from a first-order transition. The solid curves are the results of convolving the step functions with a weighting function associated with the temperature spread due to laser heating. (see Ref./15/)

Since this is a zero field transition between two ordered magnetic phases, the transition is first-order by symmetry /33/. For $T=1.9$ K the sharp peak at $\omega_{\text{LO}}(2\vec{q}_L/3) = 169 \text{ cm}^{-1}$ is characteristic of the three-sublattice ferrimagnetic phase as discussed above. For $T=1.7$ K, however, this peak is quenched and a sharp line at $\omega_{\text{LO}}(\vec{q}_L) = 153 \text{ cm}^{-1}$ emerges, corresponding to the two-sublattice antiferromagnetic phase. The observed temperature dependence of these lines is shown in figure 5b. Due to laser heating effects, a range of temperatures and thus a mixture of magnetic phases can exist in the scattering volume for each well-controlled temperature of the liquid

helium bath. To estimate the effect that laser heating would have on a first-order transition, the temperature dependence of the Raman intensity for both lines was assumed to have the form of a step function as shown by the dashed lines in figure 5b. The step functions were then convolved with a weighting function to account for the temperature variation across the laser beam in the sample /11,14/. The solid lines represent the results of the convolution which used a value of 0.15 K for the $1/e$ width of the weighting function and an average temperature shift of 0.15 K, while the data points are from experiment /11,14/. The results of figure 5b confirm that when heating effects are accounted for at $H=0$, the two- and three-sublattice phases are distinct and undergo a first-order transition near $T=1.8$ K.

5. Conclusion.- Although there are formidable experimental difficulties (e.g. laser heating) involved in using light scattering experiments to measure the critical exponents α (specific heat) and β (order parameter) from the temperature dependence of the broad and sharp Raman lines respectively, one can still use the Raman spectra of the europium chalcogenides to study the behavior of the spin order and fluctuations near magnetic phase transitions. In particular, the Raman sharp lines which measure the magnetic order parameter at $\vec{q} \neq 0$ can be used to examine the first- or second-order nature of the phase transitions in EuSe and EuTe as a function of both temperature and magnetic field as described in Section 4. Such a study is of interest in EuSe since there is as yet no theory which accurately accounts for the complete phase diagram of this material /21/.

Similarly, Raman experiments performed near $H=0$ and $T=T_N$ in EuTe should determine whether the order parameter changes continuously or discontinuously at the transition. Recent calculations have shown that for antiferromagnets with $d=3$ and $n=8$, the transition from the paramagnetic

to antiferromagnetic phase at $H=0$ is first order /34/. If one neglects the in-plane anisotropy, EuTe corresponds to $n=8$ and $d=3$, but no evidence has yet been presented supporting a first-order transition at $H=0$ and $T=T_N$. The Raman sharp lines measure the staggered magnetization directly and can be used to study this problem.

In addition to probing the $H=0$ effects, the sharp line Raman intensity of EuTe can be used to measure the staggered magnetization near the second-order, spin-flop to paramagnetic transition which occurs at the critical field given by /10,25/ $H=H_c(T)$. In particular, near $H_c(T)$, N is proportional to $(H_c^2(T)-H^2)^\beta$. Recent renormalization group calculations have indicated that one expects a crossover from $d=3$, $n=2$ critical behavior /27,35/ ($\beta=.36$) to mean field behavior ($\beta=1/2$) near $T \sim 0$ due to quantum effects/36/. This prediction can be tested by measuring the field dependence of the sharp line in EuTe for various temperatures. EuTe is of special interest in this regard since an experimentally accessible value of $H_c(0)$ occurs at 72 kG. Preliminary efforts in this direction have been reported in ref./7/.

Finally, one could extend both the theory and experiment discussed here to other magnetic materials. In centrosymmetric materials with one magnetic atom per chemical unit cell one expects no first-order phonon spectra, so that any observed one-phonon Raman lines can be associated with spin-phonon scattering. For example, CeSb, a magnetic material which has recently been studied using neutron scattering/38,39/ has shown many ordered sublattice structures some of which are incommensurate (or high-order commensurate) with the underlying lattice. Recent theories /37/ have predicted a "devil's staircase" behavior for the magnetic phase diagram with a large number of phases in between two commensurate ordered phases. Since both CeSb and the europium chalcogenides have the FCC struc-

ture, the symmetry of the Raman tensor is the same for both materials. Given the presence of a large excited state spin-orbit coupling, one could hope to study the spin order and fluctuations in CeSb through one phonon-one spin scattering as well.

Acknowledgements.- The author gratefully acknowledges collaborations and many useful discussions with Dr. G. Dresselhaus, Dr. R. P. Silberstein, Prof. M. S. Dresselhaus, Dr. L. E. Schmutz and Prof. B. Lax.

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