Magnetic-field-dependent Raman scattering in EuSe†*‡

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A new type of symmetry-forbidden resonant Raman scattering has been observed in the magnetic semiconductor EuSe at low temperatures and in an applied magnetic field. The most striking difference between this phenomenon and previously observed resonant Raman scattering is the observed dependence of the scattering intensity in EuSe on the magnitude and direction of the applied magnetic field. The intensity of the symmetry-forbidden scattering is observed to increase monotonically with increasing magnetic field strength for fields as high as 100 kG, increasing most rapidly in the low-field regime below the saturation magnetization. The scattering intensity is found to depend on the angle between the polarization of the incident light and the magnetic field, with the maximum scattering intensity observed when the incident beam is polarized normal to the applied magnetic field. This symmetry-forbidden scattering is observed only for temperatures below the magnetic critical temperature, $T < T_C$. The observed scattering in EuSe exhibits a resonant-type behavior similar to that observed in symmetry-forbidden resonant Raman scattering in nonmagnetic materials in terms of (1) a strong dependence of the scattering intensity on the laser excitation energy, (2) the peak intensity occurring at the zone-center LO-phonon frequency ω_{LO}, (3) observation of harmonic structure at multiples of ω_{LO}, (4) relatively large scattering intensity and narrow linewidth, and (5) occurrence only in the diagonal scattering geometry where the incident and scattered light are similarly polarized. To interpret the results of this new type of symmetry-forbidden resonant Raman scattering, we have considered various models for resonant Raman scattering in which the effects of an external magnetic field on the electronic structure of EuSe are treated explicitly. We have found all existing models to be inadequate for the explanation of the experimental data.

I. INTRODUCTION

We have observed a novel form of symmetry-forbidden resonant Raman scattering in the magnetic semiconductor EuSe at low temperatures and in an applied magnetic field.[1] Our results differ considerably from resonant Raman-scattering results reported in nonmagnetic semiconductors such as CdS,[2,3] insofar as we observe an extremely strong dependence of the symmetry-forbidden Raman scattering on the strength and direction of the applied magnetic field. Because of this strong magnetic field dependence, we find that this symmetry-forbidden LO-phonon-scattering phenomenon cannot be understood in terms of existing theories for resonant Raman scattering.

In contrast with the broad-line scattering observed in all the europium chalcogenides for $T > T_C$,[4] the anomalous symmetry-forbidden Raman scattering is observed in EuSe only at low temperatures and in the presence of an applied magnetic field. The anomalous Raman scattering occurs at the LO-phonon frequency and is considerably sharper and more intense than the broad-line scattering which is observed below the LO-phonon frequency. We have studied the dependence of this anomalous "sharp-line LO-phonon" scattering in EuSe on magnetic field, temperature, light polarization, laser excitation energy, and sample characteristics. The results of this study are presented in this paper.

Because the anomalous LO-phonon scattering is observed only at temperatures below the magnetic critical temperature T_C of EuSe and in magnetic fields large enough to produce major changes in the spin configuration and electronic structure of EuSe, we present in Sec. II a brief discussion of the magnetic and electronic properties of this material. We also consider some of the theoretical aspects of symmetry-forbidden Raman scattering to provide background for a meaningful presentation of the experimental results in Sec. IV. We then show in Sec. V that our results cannot be understood in terms of existing models for symmetry-forbidden (i) defect-induced Raman scattering,[5] (ii) surface-electric-field-induced

Raman scattering,[6] or (iii) resonant Raman scattering in nonmagnetic semiconductors.[2,3] The paper concludes with a discussion of possible approaches to the understanding of our results and of their implication on resonant Raman scattering in magnetic and nonmagnetic systems.

II. BACKGROUND

Europium selenide crystallizes in the face-centered-cubic structure. Since every atom in the fcc structure sits at a center of inversion symmetry, first-order Raman scattering from odd-parity phonon modes is symmetry-forbidden in EuSe.[4]

A. Electronic and magnetic properties of EuSe

The electronic properties of EuSe in the visible region of the spectrum are dominated by transitions from the magnetically active and spatially localized Eu^{++} $4f^7$ states to $4f^6\,5d$ excited states. Insulating EuSe is transparent in the near infrared. As the phonon energy is increased, the $4f^7 \rightarrow 4f^6\,5d$ transitions first appear at an energy of about 1.8 eV. The strength of the $4f^7 \rightarrow 4f^6\,5d$ transitions is indicated by the fact that at about 2.2 eV, the absorption coefficient of EuSe, due largely to these transitions, is in excess of 10^5 cm^{-1}.[7]

EuSe is identified as a moderately ionic solid because of the significant splitting of the zone-center LO- and TO-phonon-mode frequencies.[8] Measurements of the high- and low-frequency dielectric constants of EuSe and of the infrared absorption and reflectivity show that the zone-center LO- and TO-phonon frequencies are split by over 50 cm^{-1} with $\omega_{TO} = 127$ cm^{-1} and $\omega_{LO} = 182$ cm^{-1} at room temperature. Because of the ionic contribution to the binding of EuSe, one expects that there will be both deformation-potential and Fröhlich-interaction contributions to the electron-phonon interaction in EuSe.

Because of the importance of the $4f^7$ states in determining the magnetic properties of EuSe, there is strong coupling between the electronic and magnetic properties of EuSe. The optical properties of EuSe undergo large changes as the temperature of EuSe is reduced below its magnetic critical temperature and as an external magnetic field is applied. Examples of these changes are (i) the observation of a large shift of the absorption edge to the red for $T \lesssim 5$ K and (ii) the splitting of the reflectivity band associated with the $4f^7 \rightarrow 4f^6\,5d$ transitions in the presence of an applied magnetic field and at low temperatures. Considerable work has been done on the magnetic field dependence of the optical properties of EuSe.[9]

The magnetic structure of europium selenide is complicated, showing a multiplicity of magnetic phases at low temperatures. EuSe is paramagnetic for $T > 4.8$ K. For $T < 4.8$ K, EuSe is antiferromagnetic. However, below 2.8 K, EuSe shows a ferrimagnetic phase. Recently, experimental evidence of yet another antiferromagnetic phase for $T < 1.8$ K has been reported.[10] Changes in the magnetic structure of EuSe can be induced by the application of an external magnetic field. In particular, for $T < 4.8$ K, a magnetic field of less than 20 kG is sufficient to drive EuSe ferromagnetic.

B. Resonant Raman scattering

Resonant Raman scattering has been observed from a variety of common semiconductors.[2] Both symmetry-allowed and symmetry-forbidden resonant scattering has been observed. The symmetry-forbidden scattering observed in ionic semiconductors such as CdS has been characterized by (i) a strong resonant enhancement of the cross section in the vicinity of the fundamental absorption edge, (ii) the appearance of forbidden scattering at the zone-center LO-phonon frequency ω_{LO}, (iii) harmonic structure found only at multiples of ω_{LO}, and (iv) the observation of symmetry-forbidden lines only in the diagonal scattering geometry $(\vec{E}_s \| \vec{E}_i)$.

Theoretical expressions for the resonant Raman tensor have been calculated for situations where the scattering process is dominated by contributions from free electrons and holes,[11] from free excitons,[12] from bound excitons,[13] and from polaritons.[14] In all cases, the Raman tensor shows singular behavior when the excitation energy is close to the energy separation between resonant electronic states. Loudon has shown[11] that the expression for the Raman tensor R^l_{ij}, which describes scattering polarized in the jth direction from an l-branch phonon excited by an incident beam polarized in the ith direction, will have a double-energy denominator, so that the Raman process can be viewed as arising out of third-order time-dependent perturbation theory. The double-energy denominator causes the scattering cross section to diverge when either the excitation energy is equal to the energy of a resonant electronic transition or the scattered energy satisfies the resonance condition. In addition to this resonant enhancement of the Raman tensor, Hamilton[15] pointed out that anomalies could be expected in the Raman selection rules for LO-phonon processes involving resonant excitations through the Fröhlich interaction. The cancellation of the electron and hole contributions to the electron-phonon interaction arising from the Fröhlich interaction at $\vec{k} = 0$ implies that the Fröhlich contribution to the Raman cross section for LO-phonon scattering has to be evaluated for a finite wave vector. Hamilton[15] pointed out that under resonant condi-

tions, Raman scattering from phonons of finite wave vector could be appreciable and that this scattering would be described by selection rules other than those normally obeyed by Raman scattering from zone-center LO phonons. In the finite-wave-vector limit, the Raman tensor for scattering from LO phonons via the Fröhlich interaction will have the transformational properties of a product of four vectors: the incident electric field vector $\vec{E}_i$, the scattered electric field vector $\vec{E}_s$, the phonon polarization vector $\vec{u}_k$, and the phonon wave vector $\vec{k}$. This is in contrast to the case of a long-wavelength limit where the phonon wave vector is always equal to zero. In the case of a finite wave vector, Raman scattering from odd-parity phonons becomes symmetry allowed.

Scattering from phonons of finite wave vector can be substantial under resonant conditions. In both EuS and EuSe, the 5145-, 4965-, and 4880-Å lines of the argon-ion laser overlap the $4f^7 \rightarrow 4f^6 5d$ absorption band. Magnetoreflectance studies have been interpreted in terms of a magnetic field dependence of the $4f^7$–$4f^6\,5d$ separation.[9] Such a mechanism could give rise to a resonant Raman process which is sensitive to an externally applied magnetic field.

III. EXPERIMENTAL DETAILS

The 5145-, 4965-, and 4880-Å lines of an argon-ion laser were used to excite the Raman spectra of EuSe. The laser lines correspond to energies of about 2.39, 2.48, and 2.54 eV, respectively. Since EuSe is opaque in this photon-energy region, the Raman measurements were made in the backscattering geometry. Measurements were made at room temperature, near 80 K, for $20 < T < 40$ K, and $1.7 < T < 2.0$ K. Magnetic fields up to 15 kG were available using a 9-in. Varian magnet, and fields as high as 100 kG were available using a radial-access Bitter solenoid. Measurements of the magnetic-field-dependent Raman spectra were made with the Varian magnet in both the Faraday and Voigt configurations, and using a Spex Model 1400 double monochromator, equipped with a pair of 600-lines/mm diffraction gratings blazed at 0.5 μm. Measurements using the Bitter solenoid were made in the Voigt configuration using a similar monochromator with a pair of 600-lines/mm diffraction gratings blazed at 1.0 μm and operating in second order. With the Faraday configuration, the maximum available magnetic field was 8 kG, while in the Voigt geometry, fields up to 14 kG were provided by the Varian magnet and up to 100 kG by the Bitter solenoid. In all other respects, conventional techniques were employed in carrying out the Raman-scattering measurements.[16]

Our EuSe samples were all cleaved from boules which were grown from the melt and contained large single-crystal regions. Most of the crystals were grown in europium-rich solutions. The Raman spectra were studied both for insulating samples that were transparent in the red and for strongly conducting samples that were completely metallic in appearance. All measurements were made on (100) cleaved surfaces.

IV. EXPERIMENTAL RESULTS

No evidence of sharp-line Raman scattering similar to that observed in nonmagnetic semiconductors such as CdS at the LO-phonon frequency and its harmonics was observed in EuSe for $T > 20$ K under any circumstances.

However, when the EuSe samples were cooled below the λ point of liquid helium, a number of small changes were observed in the Raman spectra. On the other hand, when a magnetic field was applied to the cooled sample, *major* changes in the spectra were observed and strong sharp-line LO-phonon structures began to emerge. The determination of the characteristic properties of this sharp-line scattering in the magnetic semiconductor EuSe is the central focus of the present study.

Considerable variation was observed in the behavior of the low-temperature magnetic-field-dependent Raman spectra between different samples of EuSe. We begin by explicitly considering the behavior of one particular sample of EuSe at low temperatures and in a magnetic field. We will then discuss the various types of sample dependences that were observed.

For $T > T_C$ the Raman spectrum of EuSe consists of the broad first-order Raman line and its harmonics that we have described elsewhere.[1,17] The reduction of the sample temperature to below 2.0 K (which lies below most of the critical temperatures of EuSe) produces a small but significant change in the first-order Raman spectra of EuSe, as is seen in Fig. 1, by comparing the first-order Raman lines observed at 1.8 K ($T < T_C$) and at 80 K ($T > T_C$); both traces were taken in zero applied magnetic field. The first-order Raman line at 1.8 K indicates a shoulder near ω_{LO}, which is not observed at 80 K. The shoulder is perhaps more clearly seen in the $H = 0$ trace of Fig. 2. We feel that the extra shoulder observed at 1.8 K corresponds to a relatively narrow line (as compared with the linewidth of the first-order Raman line observed in EuSe for $T > T_C$). This narrow line is centered at about 185 cm^{-1}, which is close to the room-temperature zone-center LO-phonon frequency $\omega_{LO} = 182$ cm^{-1}.[8] Because of the low intensity of the shoulder in zero magnetic field, no detailed study was made of the characteristics of this

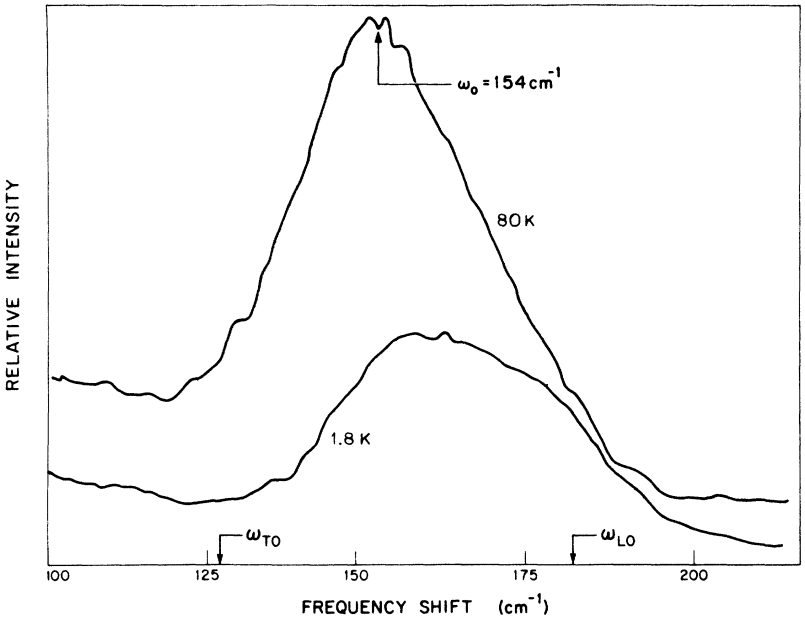

FIG. 1. First-order Raman spectrum of EuSe at $T = 80$ K ($T > T_C$) and $T = 1.8$ K ($T < T_C$) in zero magnetic field under 5145-Å laser excitation. The zone-center LO- and TO-phonon frequencies of EuSe at 300 K are indicated in the figure. Note in the 1.8-K trace the shoulder in the vicinity of ω_{LO}.

extra line with regard to its polarization dependence, temperature dependence, excitation-energy dependence, etc. It is, however, found that the shoulder seen at 1.8 K for $H = 0$ kG under 5145-Å laser excitation is not seen under 4880- or 4965-Å excitation under similar conditions.

The shoulder observed weakly in zero magnetic field is of interest because we have determined that its intensity is extremely magnetic field dependent. Figure 2 shows the Raman spectra of EuSe in the region of the zone-center LO-phonon frequency at 1.8 K under 5145-Å laser excitation for $H = 0$, 2.5, and 15 kG. In this figure it is seen that a new sharp structure is introduced by the magnetic field at the LO-phonon frequency. This sharp structure is so intense that it completely dwarfs the broad-line structure which dominates the zero-field Raman spectrum. In contrast to the broad-line scattering which is quenched by the application of a magnetic field, the new sharp LO-phonon structure is strongly enhanced by the magnetic field. The magnetic-field-enhanced LO-phonon line is a relatively narrow line, having a half-width of about 7–8 cm^{-1} in contrast with the 35 cm^{-1} half-width of the broad-line structure, which is quenched by the magnetic field.

To demonstrate the magnetic field enhancement of the sharp-line structure, we plot in Fig. 3 the intensity of the first-order LO-phonon line at 1.8 K as a function of applied magnetic field for $0 < H < 100$ kG using 5145-Å laser excitation. As can be seen, the intensity of the LO-phonon line shows a strong dependence on applied magnetic field, increasing by over two orders of magnitude as H is varied between 0 and 15 kG. Even though the saturation magnetization of EuSe is ~13.6 kG, we find that the intensity of this first-order LO-phonon line continues to increase as a function of increasing

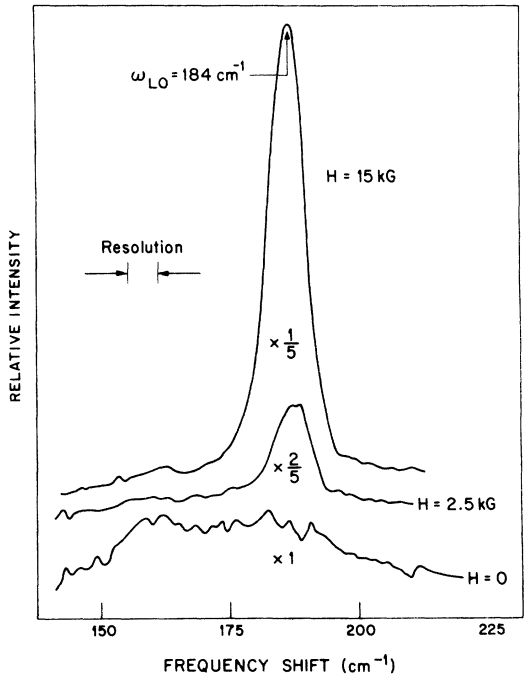

FIG. 2. First-order Raman spectra of EuSe at $T = 1.8$ K for H = 0, 2.5 kG, and 15 kG using 5145-Å laser excitation, and $\vec{E}_s \| \vec{E}_i$.

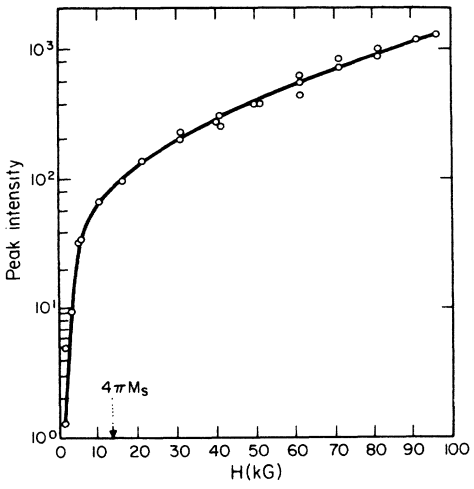

FIG. 3. Magnetic field dependence of the peak intensity of the first-order LO-phonon line in EuSe at $T=1.8$ K under 5145-Å laser excitation, using the Voigt geometry with $\vec{E}_s \| \vec{E}_i$.

H, with the increase in intensity amounting to about one order of magnitude as H increases from $4\pi M_s \sim 13.6$ to 100 kG.

In the presence of a magnetic field, it is found that the intensity of the sharp-line LO-phonon scattering is strongly dependent on the laser excitation energy. It is convenien to study this dependence on excitation energy in terms of a relative intensity defined by the ratio of the intensity of the sharp-line LO-phonon scattering to the intensity of the zero-field broad-line scattering which is independent of excitation energy.[1] As can be seen in Fig. 4, the relative intensity of the magnetic-field-enhanced structure varies by over two orders of magnitude as the excitation wavelength is decreased from 5145 to 4880 Å. The data in Fig. 4 are presented for three different values of magnetic field. The strong dependence of the relative scattering intensity on the excitation energy appears to be independent of applied magnetic field. The small number of available excitation energies from our argon-ion laser prevents us from drawing quantitative conclusions concerning the excitation-energy dependence of this LO-phonon scattering process, other than that the process is *strongly* excitation-energy dependent.

Within the limited resolution of the experiment, we find that the magnetic field dependence of the intensity of this LO-phonon line is qualitatively similar for various available laser excitation energies, and this is illustrated in Fig. 5. Here we show the magnetic field dependence of the relative intensity of the LO-phonon line for both 4880- and 5145-Å laser excitation. Because the relative intensity of the LO-phonon scattering for 4880-Å excitation is almost two orders of magnitude below that for 5145-Å excitation, we can only observe the magnetic field dependence of the intensity of the first-order LO-phonon line under 4880-Å excitation for fields in excess of 10 kG.

The Raman tensor describing the magnetic-field-dependent sharp-line LO-phonon scattering depends also on the *direction* of the applied magnetic field and the polarization of the incident and scattered radiation. All of the measurements in Figs. 1–5 were made in the Voigt geometry where the magnetic field $\vec{H}$ is parallel to the surface of the sample and normal to the wave vector of the light inside the sample. For scattering in the Voigt geometry, we find that the scattered light is linearly polarized perpendicular to the applied magnetic field. The polarization of the scattered light is found to be independent of both sample orientation and of the polarization of the incident light. The intensity of the scattered light however does depend on the angle θ between the polarization of the incident light $\vec{E}_i$ and the direction of the applied magnetic field $\vec{H}$. In Fig. 6, we show the variation of the intensity of the first-order LO-phonon scattering as a function of this angle θ. In Fig. 6, it can be seen that the intensity of the scattered radiation is greatest when the incident beam is polarized normal to the applied magnetic field and is almost zero when the incident beam is polarized parallel to the applied magnetic field.

Although the intensity and the polarization prop-

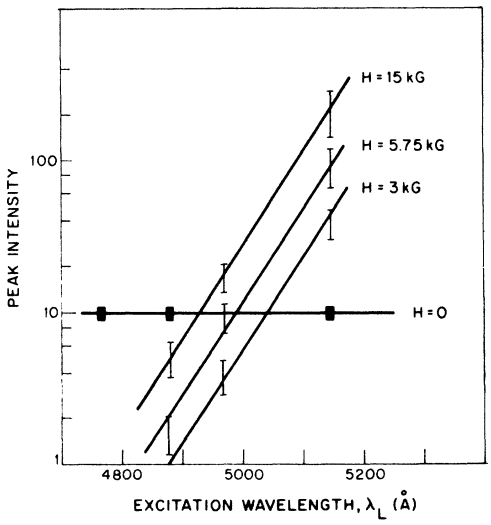

FIG. 4. Excitation wavelength dependence of the peak intensity of the first-order LO-phonon line in EuSe at $T=1.8$ K. Data are taken for various magnetic fields in the Voigt geometry with $\vec{E}_s \| \vec{E}_i$.

erties of the sharp-line first-order LO-phonon scattering are strongly magnetic field dependent, we find that both the linewidth and the central frequency of the first-order LO-phonon line appear to be independent of the applied magnetic field for $H \leq 100$ kG.

Thus far, we have stressed the behavior of the Raman scattering observed in the region of the zone-center LO-phonon frequency in EuSe. As in the case of the broad-line scattering observed in EuS and EuSe,[1] we find that the symmetry-forbidden first-order LO-phonon scattering is accompanied by strong higher harmonics as can be seen in Fig. 7 at $2\omega_{LO}$ and $3\omega_{LO}$. Here we show the Raman spectra of EuSe at 1.8 K, $H = 15$ kG for frequency shifts of up to 600 cm^{-1} under 5145-Å laser excitation. In this figure, the Raman spectrum shows a strong second-order line at about 369 cm^{-1} and a third-order line at about 556 cm^{-1}. The higher-order lines are quite narrow and are comparable in relative width to the higher-order lines observed in resonant Raman-scattering experiments on nonmagnetic semiconductors.[2] We observe that while the first-order line in Fig. 7 has a half-width of ~7–8 cm^{-1}, the second- and third-order lines have half-widths on the order of ~12 and ~18 cm^{-1}, respectively. These values should be contrasted with the linewidths of the broad-line scattering in EuSe which are, respectively, ~35, ~50, and ~70 cm^{-1}. The higher-order Raman lines are also observed only at low temperatures and in finite applied magnetic fields and show many of the same characteristics of the first-order LO-phonon line. For magnetic fields above 3 or 4 kG, they share (i) the same magnetic field dependence with respect to their intensity, (ii) the same excitation energy dependence, and (iii) the same polarization dependence. In the case of both the fundamental and its harmonics, the linewidths and central frequencies are also independent of applied magnetic field. As might be expected from the negligible phonon occupation number at low temperatures, no anti-Stokes LO-phonon scattering was observed at 1.8 K in EuSe.

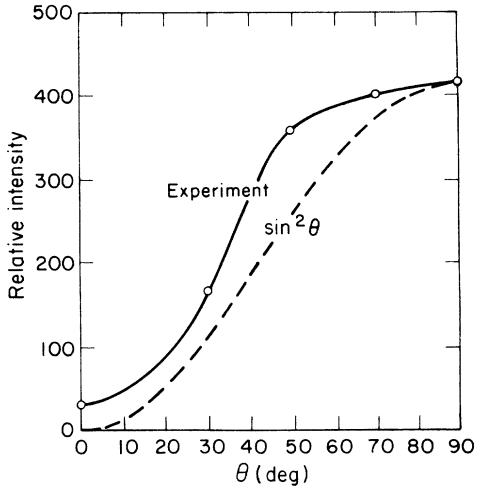

FIG. 6. Peak intensity of the first-order LO-phonon line in EuSe as a function of the angle θ between $\vec{E}_i$ and $\vec{H}$. The data are taken under 5145-Å laser excitation and in the Voigt geometry with $H = 15.5$ kG and $T = 1.8$ K.

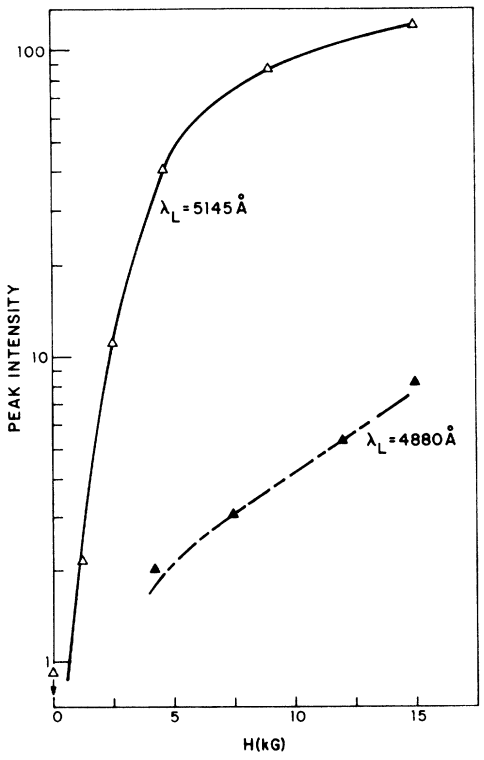

FIG. 5. Magnetic field dependence of the peak intensity of the first-order LO-phonon line in EuSe at $T = 1.8$ K under 4880- and 5145-Å laser excitation. All data are taken in the Voigt geometry for $\vec{E}_s \| \vec{E}_i$.

We have mentioned that there is considerable variation from sample to sample with regard to certain aspects of the sharp-line magnetic-field-dependent scattering observed in EuSe. The chief variations were in the linewidths and quantitative magnetic field dependence of the intensity of the first- and higher-order LO-phonon lines and in the relative intensities of the first- and higher-order LO-phonon lines. To contrast the spectra obtained from different EuSe samples, we show in Fig. 8 the spectrum observed in a conducting sample which is metallic in appearance. This spectrum was obtained at a temperature of 1.8 K using the 5145-Å laser line. The spectra shown in the

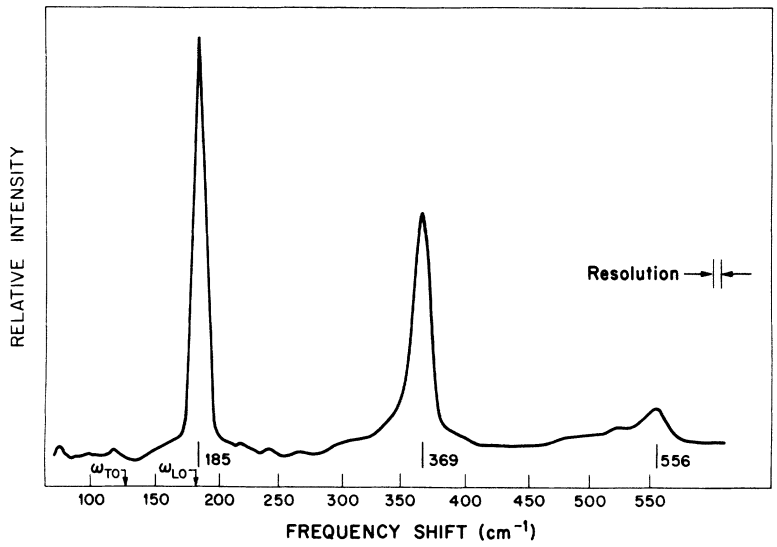

FIG. 7. Raman spectrum of an insulating sample of EuSe at $T=1.8$ K, $H=15.5$ kG, and under 5145-Å laser excitation, showing peaks at ω_{LO} and its higher harmonics.

previous figures were obtained from a high-purity sample of EuSe that is transparent in the red and is electrically insulating. As can be seen in Fig. 8, the second-order scattering for the conducting sample is actually more intense than the first-order scattering. In addition, the half-widths of the first-, second-, and third-order Raman lines are considerably greater than those obtained for the insulating sample shown in Fig. 7.

The magnetic field dependence of the first-order LO-phonon intensity of a conducting sample at 1.8 K and under 5145-Å excitation is shown in Fig. 9. While the magnetic field dependence of the first-order LO-phonon scattering shown in Fig. 9 is qualitatively similar to that shown for the insulating sample in Fig. 3, substantial quantitative differences are observed. In particular, the magnitude of the magnetic-field-dependent enhancement is considerably greater for the insulating sample shown in Fig. 3 as compared with that for the conducting sample shown in Fig. 9.

V. THEORETICAL CONSIDERATIONS

Symmetry-forbidden Raman scattering in a crystalline solid has been identified with either disorder mechanisms or with higher-order scattering processes. In particular, symmetry-forbidden Raman scattering from LO-phonon modes has been attributed to (i) a surface interface or lattice defects, which reduce the symmetry of the host lattice,[5] (ii) spin-disorder effects which lower the symmetry of the electronic wave functions of a magnetic crystal,[17] and (iii) finite-wave-vector effects which change the symmetry properties of the Raman tensor for LO-phonon scattering.[15] Since the sharp-line LO-phonon scattering is observed only at low temperatures and in the magnetically ordered state, spin-disorder effects cannot be responsible for the sharp-line LO-phonon scattering observed in EuSe.

Similarly, it is unlikely that the observed spectra are due either to the presence of random defects in the lattice or to the existence of a surface interface.[6] In the case of the defect mechanism, the observed scattering does not exhibit the expected temperature independence of the scattering intensity, insofar as the observed effect is a low-temperature phenomenon. Furthermore, the observed scattering intensity does not follow the expected variation from one sample to another, since samples with *greater* defect densities yield *lower* rather than higher scattering intensities. In addition, the general appearance of the observed spectra differs from typical Raman spectra identified

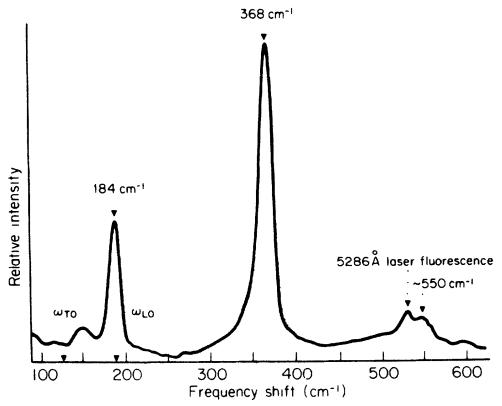

FIG. 8. Raman spectrum of a conducting sample of EuSe at $T=1.8$ K, $H=15.5$ kG and under 5145-Å laser excitation, showing peaks at ω_{LO} and its higher harmonics.

with the presence of defects in nonmagnetic cubic solids.[5]

Because of the observed magnetic field and temperature dependence of the sharp-line LO-phonon scattering, it is unlikely that the scattering mechanism is due to an electric field associated with a crystal-surface interface. Such electric-field-induced scattering processes would be expected to be only weakly dependent on temperature and magnetic field. Furthermore, the sha p-line LO-phonon spectrum observed in EuSe differs in general appearance from that reported for surface field-induced resonant scattering,[6] particularly with regard to the relatively large intensities of the higher harmonics observed in the sharp-line spectrum of EuSe. Because the symmetry-forbidden sharp-line spectrum is observed in both insulating and conducting samples of EuSe, any model based on an induced electric field at the crystal surface is rendered less plausible.

It is, however, tempting to explain our data in terms of a resonant scattering process via the Fröhlich interaction,[15] because of the strong dependence of the observed scattering intensity on the excitation energy. In this context, the strong magnetic field dependence of the scattering intensity would be attributed to resonant scattering effects associated with the magnetic field dependence of the electronic structure of EuSe. In particular, the magnetic field is known to tune the E_1'' reflectivity peak in EuSe into the position of the first-order LO-phonon line excited by the 5145-Å laser line.[9] Although this model would successfully explain certain resonant aspects of the experimental data, it nevertheless fails to explain a number of important features of the experimental observations. The most important of these is the fact that the intensity of the forbidden Raman scattering increases monotonically with increasing magnetic field, for magnetic fields in excess of the saturation magnetization, $4\pi M_s = 13.6$ kG. At these high magnetic fields, Pidgeon *et al.*[9] show that there is no longer any magnetic field dependence of the position of the E_1'' reflectivity peak.[9] Assuming that the resonant cross section for 5145-Å excitation is dominated at low temperatures by the contribution from the E_1'' peak and that the E_1'' peak is due to a transition between a pair of narrow levels (the $4f^7$, $4f^6\,5d$ levels), we obtain for the magnetic field dependence of the first-order LO-phonon-scattering cross section the results shown in Fig. 10. (Relaxation of the assumption that the transition occurs between sharp levels would produce a smearing-out of the magnetic field dependence shown in the figure.) In constructing Fig. 10, we have used the Loudon expression for the strength of the Raman tensor and have assumed that the scattering cross section is dominated by the term in the Raman tensor containing two resonant denominators.[11] According to the results of Pidgeon *et al.*[9], the magnetic field dependence of the E_1'' peak saturates at about 20 kG, and consequently the magnetic field dependence of the predicted forbidden scattering intensity shown in Fig. 10 also saturates at about 20 kG. As can be seen by comparison of Figs. 3 and 10, the experimental results do not exhibit saturation behavior above 20 kG. This resonant Raman-scattering model in which the magnetic field tunes the energy levels into resonance with the excitation energy also appears to fail quantitatively at lower magnetic fields. The analysis of the low-field data is considerably complicated by uncertainties with respect to the demagnetizing fields associated with the particular geometries we have used.

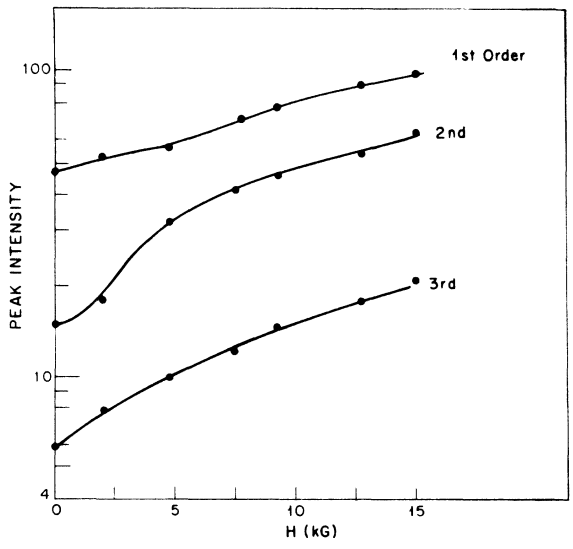

FIG. 9. Magnetic field dependence of the intensity of the LO-phonon lines observed in a conducting sample of EuSe at $T = 1.8$ K and under 5145-Å laser excitation.

A further difficulty with the simple resonant-scattering model is associated with the behavior of the reflectivity spectra of EuSe for $T > T_C$, and in both zero and applied magnetic fields. From reflectivity and absorption measurements, it is found that the fundamental edge of EuSe shifts to *lower* energies as the temperature is reduced below T_C.[7,9] It is furthermore found that the application of a magnetic field at low temperatures shifts the E_1'' peak to *higher* energies, such that the magnetic-field-induced shift is comparable to and in the opposite direction of the temperature-induced shift. In particular, for $T = 20$ K, and in zero magnetic field, there exists a substantial overlap between the energy range corresponding to the reflectivity maximum of EuSe and the 5145-Å laser

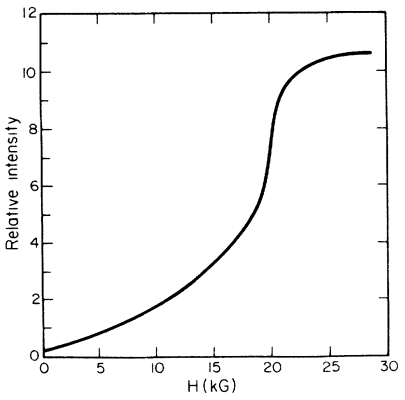

FIG. 10. Calculated magnetic field dependence of the LO-phonon scattering intensity. Resonant effects are here associated with the magnetic field dependence of the E_1' maximum (Ref. 9).

line. If the symmetry-forbidden resonant scattering is simply attributed to this energy overlap, then symmetry-forbidden resonant scattering should also be observed in EuSe for $T > T_C$ and both in zero and applied magnetic field, which is not supported by experiment. It should be pointed out that the failure of the resonant-scattering model to explain the magnetic field dependence of the first-order LO-phonon intensity rules out both the direct application of the Hamilton[15] model for symmetry-forbidden LO-phonon scattering and also the possibility that the forbidden first-order LO-phonon scattering is due to either resonant defect-induced[13] or resonant surface field-induced scattering.[6]

Several arguments can be given to support the idea that the applied magnetic field must be considered *explicitly* in any theoretical explanation of the sharp-line LO-phonon scattering in EuSe. In the discussion above, it is seen that the simple resonant Raman process fails to explain both the magnetic field dependence of the intensity in the high-field region ($H > 4\pi M_s$) and the detailed dependence of the phenomenon on excitation energy. Furthermore, the simple resonant Raman process does not account for the strong dependence of the polarization selection rules on the direction of the applied magnetic field.

In treating the magnetic field explicitly, we can consider several magnetic-field-related effects. First, we consider the morphic effects of an applied magnetic field on the Raman tensor. This has been done by Anastassakis and Burstein,[18] who find that first-order Raman scattering remains forbidden under the application of a magnetic field to an fcc crystal structure.

We next consider the modifications in the dynamics of the electronic system produced by application of a magnetic field. The magnetic field is known to introduce new dynamic phenomena, such as the Hall effect; a Hall voltage appears when the electrons find themselves subjected to a Lorentz force that is proportional to the cross product of the applied magnetic field and the electronic group velocity. Recently, it has been shown that Hall-type terms can arise from the interaction of electrons in a magnetic field with fluxes of phonons and photons. The observed effect is proportional to $(\vec{q}_{\text{electron}} \times \vec{H})$ and is associated with the finite transfer of momentum between the photons or phonons and the electron gas. Thomas and Hopfield[19] studied the finite transfer of momentum from photons to excitons in such magneto-optical processes. Salanick *et al.*[20] have observed a similar transverse coupling between electrons and acoustic phonons in a magnetic field that can be described as a Hall-type process in which the electrons acquire momentum from the phonon flux.

Phenomenologically, we find that we can explain a number of the more interesting properties of the magnetic-field-dependent LO-phonon scattering in EuSe if we consider explicitly this Hall-type effect. To lowest order, this effect can be described by a perturbation of the form $\vec{p} \cdot (\vec{r} \times \vec{H})$. The magnetic field dependence of the Raman tensor can then be expressed in terms of an expansion of the Raman tensor in the magnetic interaction. In order to satisfy the symmetry requirements of the experimentally observed Raman tensor, this expansion must be considered for either finite photon or phonon wave vectors. This is reasonable since momentum must be conserved in the electron-phonon and electron-photon interactions. Within this limit, there are a number of terms in the power series expansion of the Raman tensor R_{ij}^l which depend on the cross product of the applied magnetic field with the wave vector of either (i) the incident photon $[\partial R_{ij}^l / \partial(\vec{q}_i \times \vec{H})]_0$ $(\vec{q}_i \times \vec{H})$, (ii) the scattered photon $[\partial R_{ij}^l / \partial(\vec{q}_s \times \vec{H})]_0 (\vec{q}_s \times \vec{H})$, or (iii) the scattered phonon $[\partial R_{ij}^l / \partial(\vec{k} \times \vec{H})]_0 (\vec{k} \times \vec{H})$. These terms are of particular interest to us because they yield a contribution to the Raman tensor due to both finite wave vectors and finite magnetic fields. We find that these terms are consistent with the symmetry properties observed in the sharp-line LO-phonon scattering in EuSe and yield an appropriate magnetic field dependence of the intensity of the LO-phonon scattering at high magnetic fields.

Since the Raman tensor includes a term that depends on the product of the phonon or photon wave vector and the applied magnetic field, then the Raman cross section will vary as the square of the applied magnetic field at high fields. From Fig. 3, we can see that the observed magnetic field dependence of the intensity of the LO-phonon scattering

in EuSe can be reasonably described by a H^2-type functional dependence for magnetic fields in excess of the saturation magnetization of 13.6 kG. At low magnetic fields, demagnetization effects make it impossible to determine accurately the magnitude of the magnetic field within the scattering volume.

The $(\vec{q}\times\vec{H})$ dependence of the Raman tensor also accounts for the symmetry properties characterizing the sharp-line spectra which are observed when the magnetic field is along the scattered electric field. The Raman tensor in this case has the transformational properties of a product of $\vec{E}_i$, $\vec{E}_s$, $\vec{u}_q$, and $(\vec{q}\times\vec{H})$. From elementary considerations, it is expected that electronic motion along the magnetic field is insensitive to the field. Correspondingly it is found that the optical properties for photons polarized along the magnetic field do not depend on the magnitude of the field.[7] The observed dependence of the intensity of the scattering on the angle θ between $\vec{E}_i$ and $\vec{H}$ (Fig. 6) is explained by the resonance associated with the E_1'' gap. The E_1'' structure in the reflectivity is only observed for the polarization $\vec{E}_i \perp \vec{H}$, being absent when $\vec{E}_i \parallel \vec{H}$.

On the other hand, the $(\vec{q}\times\vec{H})$ model predicts that the sharp-line LO-phonon scattering should not be observed in EuSe in the Faraday configuration $(\vec{q}_i \parallel \vec{H})$. Although our measurements in this configuration have been limited to the range $H \lesssim 8$ kG and although the observed effects are much smaller than in the Voigt geometry, a weak magnetic field dependence has nevertheless been observed. We suggest that this weak field dependence be attributed to a slight misalignment of $\vec{H}$ with respect to the direction of the wave vector of either the incident or scattered light or of the direction of $\vec{k}$, the wave vector of the phonon.

The $(\vec{q}\times\vec{H})$ model makes explicit use of the resonant properties of the Raman tensor through the magnetic field tuning of the E_1'' level,[9] thereby giving rise to a strong dependence of the scattering cross section on the excitation energy and, through the tuning effect, on the applied magnetic field.

While the $(\vec{q}\times\vec{H})$ model for magnetic-field-dependent LO-phonon scattering duplicates many of the experimentally observed results, the model does suffer from a number of apparent microscopic difficulties. Since most of the magnetic field effects considered here appear to be small, it may be difficult to account for the large magnitude of the observed effect. In this model, the contribution to the Fröhlich interaction from both electrons and holes would depend on the same wave vector $\vec{k}$ of the phonon, so that it is not clear why the electron and hole contributions would not tend to cancel each other, even though we are in the finite $\vec{k}$ regime. This model, in its present form does not satisfactorily account for the absence of the effect for $T > T_C$. The answer to some of these objections may come from a more detailed utilization of the electronic structure of EuSe. Recent work on the transport properties of the europium chalcogenides have indicated that the lifetimes of the electronic state are dominated by spin-disorder scattering.[21] This phenomenon may have an important bearing on the quenching of the resonant Raman enhancement process in the paramagnetic phase of EuSe. In particular, it is conceivable that the resonant cross section for Raman scattering in zero magnetic field may be dominated by lifetime effects which would tend to "wash out" the resonance associated with the singularity in the Raman cross section. The application of a magnetic field at low temperatures would greatly reduce the spin-disorder scattering and consequently allow the observation of the resonance in the Raman cross section. The exponential magnetic field dependence of the scattering cross section observed for $H > 20$ kG may reflect the quenching of spin-disorder scattering as the energy for the excitation of long-wavelength magnons increases with increasing magnetic field.

Recently, a theoretical analysis has been carried out of the magnetic field dependence of the symmetry-allowed Raman spectrum observed in the chalcogenide spinels.[22] This work has shown the importance of magnon effects involving localized spins in the symmetry-allowed Raman scattering process in the chalcogenide spinels.[22] It is clear at this point that there is a great need for a detailed theoretical study of the sharp-line spectra in EuSe.

The observation of strong harmonic structure in the sharp-line spectra (Fig. 7) does provide further evidence that the LO-phonon scattering phenomena reported here are associated with a resonant process. Because of the uncertainties in the characteristics of the excited state of the electronic system, no attempt was made to explain the intensities of the harmonics relative to each other and to the fundamental line.

VI. CONCLUDING REMARKS

In this paper, we have reported the first observation of a magnetic-field-dependent resonant Raman-scattering process which is expected to be symmetry forbidden. The unusual dependence on temperature, magnetic field, and light polarization with respect to the magnetic field makes this an interesting phenomenon. Furthermore, the europium chalcogenides are appropriate materials in which to study symmetry-breaking resonant Raman-scattering phenomena because of the sensitive dependence of their energy gaps on applied magnetic field and because of the availability of

convenient laser sources corresponding to these energy gaps.

As presented above, the magnetic-field-dependent LO-phonon scattering should also be observable in EuSe in the vicinity of the E_1 and E_1' structures observed in the magnetoreflection spectrum.[9] Furthermore, this phenomenon should not be unique to EuSe and should be observable in the other europium chalcogenides, using appropriate laser sources. One advantage of observing a similar phenomenon in EuS would be the opportunity to study the temperature dependence of the sharp-line spectrum in the temperature region $T < T_C$, which was not possible in EuSe because of our inability to obtain reliable data in the temperature range $2.1 < T < 4.2$ K, owing to the bubbling of liquid helium I.

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