RESONANT PHONON SCATTERING IN MERCURY SELENIDE*

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(Received 17 March 1969)

The lattice thermal conductivity of HgSe is strongly depressed in the temperature region from 4 to 30 K. This could be accounted for satisfactorily only by a third-order (two-phonon) resonance scattering process. The relative magnitudes of the dominant Rayleigh scattering due to ionized Hg interstitials and of resonance scattering may be varied by different procedures for annealing HgSe.

The resonant scattering of phonons by various impurity centers in alkali halide crystals has been the subject of numerous investigations.[1] We report here the observation of a strong resonancelike scattering manifested in the thermal conductivity of mercury selenide (HgSe). Resonance effects on the thermal conductivity of cadmium chalcogenides and silicon have been noted,[2] but the data presented here for HgSe are the first that we know for covalent materials that can be explained only by the third-order (two-phonon) resonance scattering process of Wagner.[3] Fur-

ther, the relative magnitudes of Rayleigh scattering and resonance scattering may be varied by annealing the material in different atmospheres. Thus HgSe is a promising material for quantitative studies of the nature of defects in II-VI compounds that have the zinc-blende crystal structure.

In Figs. 1 and 2 are shown the results of measurements of the temperature dependence of the thermal conductivity of a single crystal of HgSe. The crystal was subjected to a different annealing procedure before each run: Run 1 was on the
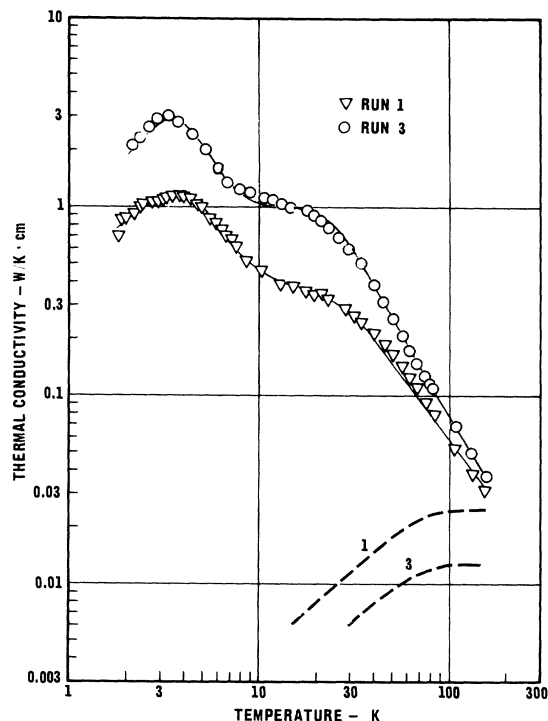

FIG. 1. Lattice thermal conductivity of HgSe as grown (Run 1) and annealed in Se vapor (Run 3). Dashed curves are calculated electronic contributions for the two runs which have been subtracted from the measured total thermal conductivity to obtain the experimental points shown. The solid curves are the theoretically computed lattice thermal conductivities.
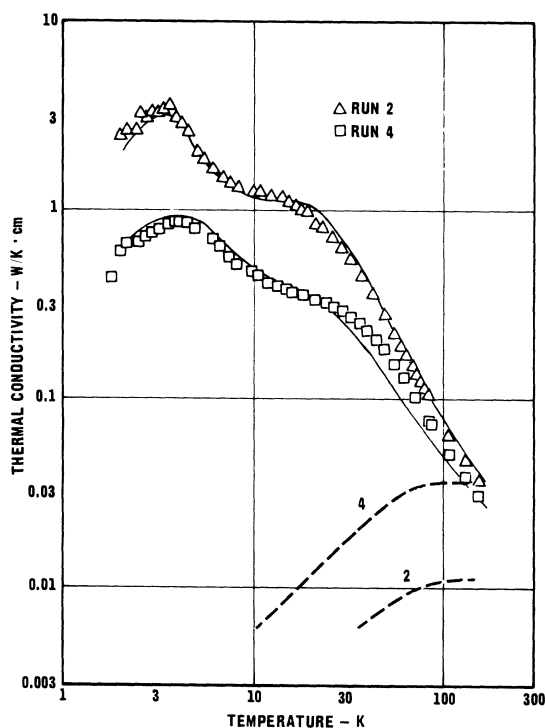

FIG. 2. Lattice thermal conductivity of HgSe annealed in vacuum (Run 2) and in Hg vapor (Run 4). Dashed curves are calculated electronic contributions for the two runs which have been subtracted from the measured total thermal conductivity to obtain the experimental points shown. The solid curves are the theoretically computed lattice thermal conductivities.

Table I. Rayleigh and resonance scattering parameters.

	Electron concentration at 77 K (cm^{-3})	A (derived) $=A_{iso}+A_{Hg}$ (10^{-43} sec^3)	A (experimental) (10^{-43} sec^3)	N (10^{21} cm^{-3})
Run 1	3.0×10^{18}	31	39	4.5
Run 2	5.3×10^{17}	5.8	6.2	4.3
Run 3	8.0×10^{17}	8.6	7.9	4.1
Run 4	6.7×10^{18}	68	61	2.3

as-grown crystal, Run 2 was on the same crystal annealed at 210°C in vacuum for 100 h, Run 3 was on the same crystal subsequently annealed at 200°C in selenium vapor for 36 h, and Run 4 was on the same crystal finally annealed at 235°C in mercury vapor for 48 h and at 255°C for 24 h. The conduction-electron concentration in each case, as deduced from measurements of the Hall coefficient, is listed in Table I. Preliminary density measurements show that the conduction-electron concentrations must primarily be due to interstitial Hg.

The lattice thermal conductivity, obtained by subtracting the electronic contribution from the total, is plotted for Runs 1 and 3 in Fig. 1 and for Runs 2 and 4 in Fig. 2. The electronic thermal conductivity was calculated from the electrical conductivity and the Wiedemann-Franz equation in which the experimental values for the Lorentz number, as determined by Aliev, Korenblit, and Shalyt,[4] were used; the calculated curves of electronic thermal conductivity also are shown in Figs. 1 and 2. In all cases there is a marked suppression of the lattice thermal conductivity between approximately 4 and 30 K (above the temperature for which the thermal conductivity is a maximum). This is most satisfactorily accounted for by the third-order resonance scattering process of Wagner.[3]

To fit the data a modification of the Callaway theory[5] was used. The inverse relaxation time was taken to be $\tau^{-1}=\tau_U^{-1}+\tau_N^{-1}+\tau_A^{-1}+\tau_L^{-1}+\tau_R^{-1}$, where $\tau_U^{-1}=B_1T\omega^2\exp(-\Theta/aT)$ represents scattering by umklapp processes, $\tau_N^{-1}=B_2T^3\omega^2$ represents normal processes, $\tau_A^{-1}=A\omega^4$ repre-

sents Rayleigh scattering, $\tau_L^{-1}=c/fL$ represents boundary scattering, and T_R^{-1} represents resonance scattering. In these expressions ω is the phonon frequency, T is the absolute temperature, Θ is the Debye temperature, c is the speed of sound, and L is the geometrical mean of the width and thickness of the sample. The constants A, B_1, B_2, a, and f are adjusted to best fit the data. The expression for τ^{-1} differs from that of Callaway by the addition of τ_R^{-1} and by the use of $\tau_U^{-1}=B_1T\omega^2\exp(-\Theta/aT)$ instead of $\tau_U^{-1}=B_1T\omega^2$ for the umklapp term. This form is that determined empirically by Slack and Galginaitis[6] for CdTe and by Walker and Pohl[7] for KCl and was found necessary for HgSe in order to fit the higher temperature data.

A resonance scattering cross section is needed which is sharply cut off on the low-temperature side. For this reason a mechanism such as that proposed by Krumhansl[8] for vacancy scattering could not fit these data. Attempts to fit the data by considering the separate contributions of longitudinal and transverse phonons by a method similar to that of Holland[9] also were not sucessful.

A mechanism which will provide a relaxation time with the proper temperature dependence has been proposed by Wagner.[3] In this process, two phonons annihilate each other to form a quantum of the resonant complex. In order for this process to be seen in the thermal conductivity, the mass or strain defect strength for the impurity must be sufficiently weak that this third-order process can dominate the usual second-order processes. Wagner has calculated the relaxation time for the process to be

$$\tau_R^{-1}=\frac{9}{16}\frac{\pi^2}{\rho}\frac{\hbar\gamma^2}{c^2}\frac{\omega_s}{\omega_a}Ng(\omega)f(\omega,T)h(\omega),$$ (1a)

$$g(\omega)=\left(1+4\frac{\omega_s}{\omega_a}\right)\ln\left\{\frac{\omega_a}{\omega_s}\frac{\omega}{\omega_s}\left(1-\frac{\omega}{\omega_s}\right)+1\right\}-4\frac{\omega}{\omega_s}\left(1-\frac{\omega}{\omega_s}\right),$$ (1b)

$$f(\omega,T)=\frac{(\omega_s-\omega)^2\exp[\hbar(\omega_s-\omega)/KT](e^{\hbar\omega/KT}-1)}{[\exp(\hbar\omega_s/KT)-1]\{\exp[\hbar(\omega_s-\omega)/KT]-1\}};$$ (1c)

$$h(\omega)=\theta(\omega-\omega_s),\quad \omega_s\leq\omega_D,$$
$$=\theta(\omega_s-\omega_D-\omega)\theta(\omega-\omega_D),\quad \omega_s>\omega_D;$$ (1d)

$$\theta(y)=1,\quad y\leq0.$$
$$=0,\quad y>0.$$

In these expressions γ is the Grüneisen constant (assumed to be 2.0), $\rho=8.266$ g/cm^3 is the crystal density, N is the product of the concentration of resonant scattering centers by the number of modes per center, ω_D is the Debye frequency, c is the average speed of sound in the material, ω_S is the average resonant frequency of the complex, and $\omega_\alpha=\alpha c$, where α^{-1} is the "radius" of the impurity.

The curves from all four runs were fitted simultaneously by a method for the estimation of nonlinear parameters due to Marquardt.[10] Only A and N were allowed to vary from run to run. The average speed of sound, $c=1.90\times10^5$ cm/sec, and the Debye temperature, $\Theta=146.6$ K, were determined by ultrasonic pulse-echo techniques at 10 MHz. The geometric mean of the width and thickness of the sample was 0.66 cm. The values for the parameters that give a least-squares fit simultaneously to the data of all four runs are $f=1.12$, $B_1=2.05\times10^{-17}$ sec/K, $B_2=1.23\times10^{-25}$ sec/K^3, $a=1.424$, $\omega_S=4.618\times10^{12}$ sec^{-1}, and $\omega_\alpha=3.3\times10^{12}$ sec^{-1}. The value for B_2 is of little significance since B_1 and B_2 are highly correlated in the fitting process. Putting $B_2=10^{-22}$ sec/K^3 produces at most a 10% change in the thermal conductivity. A separate term for the normal processes is usually omitted when the $T\omega^2\exp(-\Theta/aT)$ form is used for the umklapp processes.[6,7] The value obtained for ω_S indicates that the resonance lies within the acoustic-phonon band, that is, it is a quasilocalized mode. The value obtained for ω_α would indicate a "size" $(1/\alpha)$ of about 6×10^{-8} cm for the resonant center. However, ω_α and N are rather highly correlated in the fitting, and this value must be regarded as approximate. The values determined for A and N for each run are given in Table I. The values shown for N, the total number of resonant modes per cm^3, are certainly not realistic, even if one assumes that the complex extends to second nearest neighbors of the impurity. Er-

rors of this sort are typical of third-order processes in crystals with unit cells whose inequivalent atoms have greatly differing masses.[11] It is not known whether they are associated with dispersion,[12,13] that is, violation of the acoustic approximation, or with breakdown of the "Grüneisen approximation" [Eq. (38) of Ref. 3].

Using the expression for isotopic scattering due to Pomeranchuk[14] and Klemens[11] we find $A_{iso}=4.61\times10^{-44}$ sec^3 for HgSe. If we write $N=\beta N_R$, where N_R is the number of resonant scattering centers, and $A=A_{iso}+(3a_0^3/\pi c^3)S_{Hg}^2f_{Hg}^2+(3a_0^3/\pi c^3)S_R^2f_R$, where f_i is the mole fraction of the ith impurity, we find a best fit to the experimental values of A for $S_{Hg}=2.12$ and $\beta S_R^2<10^{-5}$ by assuming that each interstitial Hg atom contributes one conduction electron. The agreement between the experimental and derived values given in Table I is then better than 20%, and the Rayleigh scattering is due nearly entirely to the charged excess mercury. Even the most generous estimate of the number of resonant modes per center and third-order scattering errors yields $S_R<0.1$. This is consistent with Wagner's assumption that the third-order process dominates the second-order processes, that is, that the defect responsible for the resonant scattering is loosely coupled to the lattice.

The weakness of this coupling would tend to rule out, for example, Se vacancies or any charged centers. A possible source is the substitution of oxygen or tellurium for selenium in the lattice. Experiments to identify the source of the resonance scattering are now in progress.

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CRITICAL PRESSURE FOR THE METAL-SEMICONDUCTOR TRANSITION IN V₂O₃

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(Received 20 November 1968)

The metal-semiconductor transition in V_2O_3 is found to be suppressed above 26 kbar which corresponds to a volume compression of 0.9 %. The temperature and volume dependence of the resistivity of the metallic phase is consistent with semimetallic behavior and a pressure-dependent band overlap. We propose that the metal-semiconductor transition in V_2O_3 may be driven by the Coulomb attraction between electrons and holes and may be an example of an excitonic phase change.

V_2O_3 belongs to the small class of materials which undergo a metal-semiconductor transition with decreasing temperature at room pressure.[1,2] By applying pressure in excess of 26 kbar we have suppressed the low-temperature insulating phase and have studied the resistivity of the metallic phase down to 2°K. We find that both the temperature and volume dependence of the resistivity are very different from that of ordinary metals and may be explained if we assume a semimetallic state for V_2O_3 with an overlap varying as a function of pressure. These results do not support the current theoretical models[2] for the metal-semiconductor transition and lead us to propose that the metal-semiconductor transition in V_2O_3 may be an excitonic phase change.

The experiments were done in a high-pressure cryostat using a girdle die with AgCl as the pressure-transmitting medium.[3,4] The pressure calibration at room temperature was relative to the 25.4-kbar transition in a Bi wire mounted in the die, and it was assumed that at constant applied load the pressure was independent of temperature. The samples were single crystals grown by flame fusion.[5] The transition temperature of the large crystals at 1 atm was $T_0 = 176$ and 164 K on warming and cooling, respectively. However, T_0 in another sample composed of smaller chips (sample 2) was $T_0 = 119$ and 95 K. X-ray Guinier powder patterns showed that both sam-

ples had the α-corundum structure with $a = 4.948 \pm 0.002$ Å and $c = 13.97 \pm 0.01$ Å. This supports the suggestion that earlier reports of $T_0 \approx 100$ K in samples of vanadium oxide may be attributable to nonstoichiometric or impure V_2O_3.[2]

The results of T_0 vs P are shown in Fig. 1 and ρ vs T at $P > P_C$ in Fig. 2. The results were normalized to the absolute resistivities determined at 1 atm of 540 ± 100 $\mu\Omega$ cm (sample 1) and 325 ± 60 $\mu\Omega$ cm (sample 2). As the pressure was quasihydrostatic, the validity of the results was demonstrated by their reproducibility and insensitivity to the orientation of the crystals in the pressure cell.[6] Also, the pressure and temperature coefficients are in reasonable agreement with those determined under true hydrostatic pressure: $d\ln\rho/dT = +0.0018 \pm 0.0001$ K^{-1} (sample 1), $+0.0012 \pm 0.002$ (sample 2), and $+0.0023$ (hydrostatic)[7]; $d\ln\rho/dP = -0.010 \pm 0.002$ kbar^{-1} (sample 1), -0.005 ± 0.001 (sample 2), -0.005 and -0.006 (hydrostatic $- \rho_{33}$ and ρ_{11}, respectively).[7] These coefficients refer to $T = 298$ K and $P \approx 25$ kbar except for the hydrostatic temperature coefficient, where $P = 1$ atm. Repeated cycling through the transition does lead to some sample deterioration as T_0 determined at 1 atm after the pressure experiment is ≈ 10 K lower (Fig. 1).

The Clausius-Clapeyron equation relates the pressure dependence of a first-order transition to the entropy and volume changes at the transi-