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PHYSICAL REVIEW B

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Thermal Conductivity of II-VI Compounds and Phonon Scattering by Fe^{2+} Impurities

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The thermal conductivities κ of over twenty different single crystals of synthetic ZnO, ZnS, ZnSe, ZnTe, CdTe, and of natural, cubic ZnS have been measured from temperatures of 3 to 300 K. The results for the undoped crystals above 30 K can be scaled using the parameter $\bar{M}\delta\Theta^3$, where \bar{M} , δ , and Θ are the average mass, interatomic spacing, and Debye temperature, respectively. A comparison of these results with those in the literature for BeO, CdS, CdSe, HgSe, HgTe, Si, Ge, GaAs, and InSb show that the same scaling parameter applies for most of them. The compounds HgSe and HgTe exhibit anomalously low κ values. Crystals doped with Fe^{2+} show a resonant-type one-phonon scattering from the five low-lying energy levels of this $3d^6$ ion. Group theory shows that the strongest scattering occurs for phonons of energy 2Δ , where Δ is the interlevel spacing of the Fe^{2+} ion.

I. INTRODUCTION

The present work is a review of the thermal conductivity of undoped II-VI compounds with new data on ZnO, ZnS, ZnSe, ZnTe, and CdTe. With this knowledge of the behavior of pure crystals, the extra phonon scattering produced by Fe^{2+} -ion impurities in ZnS and CdTe has been studied.

A. Pure Crystals

The II-VI compound with the highest thermal conductivity κ is BeO. Results for BeO have recently been published,¹ and will not be reviewed here. Some comments on the κ of BeS have also been made.¹ Nothing is known about the κ of BeSe or BeTe. The κ of ceramic samples of $\text{ZnO}^{2,3}$ has been published, as well as a measurement⁴ of the anisotropy of its κ . In addition there are some unpublished results of Martin and Wolf⁵ and Pohl.⁶ Pohl's results are reported here. There is one report⁷ in the literature for a single crystal of ZnS, as well as two^{8,9} for ZnSe. The κ of ZnTe has been reported¹⁰⁻¹² several times. For the Cd compounds there exists a lot of work¹³⁻¹⁸ on CdS, and some work^{19,20} on CdSe. The work on CdTe has been

reviewed,²¹ but a number of papers^{9,13,21-26} on CdTe were not included in that review. Of these references, three (Refs. 13, 25, and 26) give κ values in reasonable agreement with Slack and Galginaitis.²¹

Numerous measurements of κ have been made for the compounds HgSe^{10,11,20,27-32} and HgTe.^{10-12,20,33-36} These κ results are more complicated because there is an electronic as well as a lattice contribution to κ at 300 K. Both HgSe and HgTe are classed as semimetals instead of semiconductors.

Note that the compounds CdO, HgO, and HgS have been omitted because they do not possess the adamantite (diamondlike) crystal structure.

B. Crystal Doped with Fe^{2+}

Previous measurements^{21,37-47} have shown that substitutional Fe ions can drastically lower the thermal conductivity of crystals of Ge,³⁷ $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$,³⁸ CdTe,^{21,42} MgCr_2O_4 ,³⁹ MgAl_2O_4 ,^{40,41} ZnS,⁴² KZnF_3 ,⁴³ and MgO.⁴⁴⁻⁴⁷ In these crystals the Fe^{2+} ions have either tetrahedral^{21,39-42} or nearly octahedral^{38,43-47} coordination with their nearest neighbors. The interaction of the phonons with the Fe^{2+} ions appears to be strong for

both types of coordination. In the tetrahedral environment the phonon interaction is believed to take place²¹ by means of phonon absorption that produces upward transitions between low-lying energy levels of the *d*-shell electrons of the isolated Fe²⁺ ions. A resonant scattering occurs when the phonon energy is equal to the interlevel spacing. The existence of a total of five low-lying levels has been determined for tetrahedral Fe²⁺ in ZnS,⁴⁸⁻⁵² CdTe,^{48,53,54} and MgAl₂O₄⁴⁸ by optical techniques in the near and far infrared. In these three crystals the levels are, to a first approximation, all equally spaced by an interlevel spacing energy Δ . Let an equivalent temperature T_E be defined by

$$kT_E = \Delta, \quad (1)$$

where k = Boltzmann's constant. The optical results give values of $T_E = 19, 21.6,$ and 26.8 K for MgAl₂O₄, ZnS, and CdTe, respectively. The value of T_E for CdTe is based⁵³ on $\Delta = 18.6 \text{ cm}^{-1}$ although Vallin⁵⁴ has suggested that a better value is $\Delta = 20.8 \text{ cm}^{-1}$ if Jahn-Teller effects are properly accounted for. In either case it is clear that for both ZnS and CdTe the four excited levels lie in a convenient energy range between the boiling point of liquid helium at 4.2 K and room temperature at 300 K.

Preliminary thermal conductivity measurements on Fe²⁺-doped CdTe²¹ and ZnS⁴² between 3 and 300 K have already shown that the phonon scattering effects of the Fe²⁺ ions lie between 3 and 100 K. Thus, the present measurements on ZnS and CdTe cover this temperature range. In order to accurately determine the effects of small concentrations of Fe on the thermal conductivity κ it is necessary to know the behavior of κ versus temperature T for pure ZnS and CdTe. It is for this reason that κ versus T has been measured for several other undoped II-VI compounds in this present study.

II. SAMPLES

The samples used in the present series of experiments were natural and synthetic crystals of cubic and hexagonal ZnS and cubic CdTe. Several synthetic crystals of ZnO, ZnS, ZnSe, and ZnTe were also studied in order to establish a reasonable thermal-conductivity-vs-temperature curve for the pure compounds. All of these samples are listed in Table I. The impurity analysis was carried out by a combination of colorimetric optical absorption measurements on various aqueous solutions for the Fe concentration, and by emission spectroscopy for the other trace impurities. The Fe concentration in Table I is also given in terms of $\log_{10} x$, where x is the mole fraction of iron chalcogenide present, e. g., Zn_{1-x}Fe_xS. The synthetic samples of the Zn

compounds are all quite pure, and, in particular, have low Fe concentrations. The highest concentration is $4 \times 10^{17} \text{ Fe/cm}^3$. The doped ZnS crystals were all natural cubic crystals containing Fe as the dominant impurity. Natural crystals were chosen for study since they are readily available, and since it is difficult to grow large crystals of synthetic, cubic ZnS. The CdTe crystals were all synthetic, and both high-purity and Fe-doped crystals were studied. Thus, it has been possible to study the effects of Fe impurities in both natural and synthetic crystals.

The optical absorption properties of several of the Fe-doped crystals listed in Table I have been published,⁴⁸⁻⁵⁴ and the sample numbers in the present paper agree with those in the previous publications.

III. APPARATUS

The thermal conductivity of the samples was measured in an apparatus that has previously been described.⁵⁵ The measurements were made from 3 to 300 K by a steady-state technique using gold-cobalt versus manganin thermocouples. The samples were cut in the shape of rods of length L and effective diameter D given in Table I. The effective diameter of the rods D , which are usually square in cross section, is such that the cross-sectional area is $\frac{1}{4}\pi D^2$. This value of D is important in determining the boundary scattering limit for the thermal conductivity below 5 K.

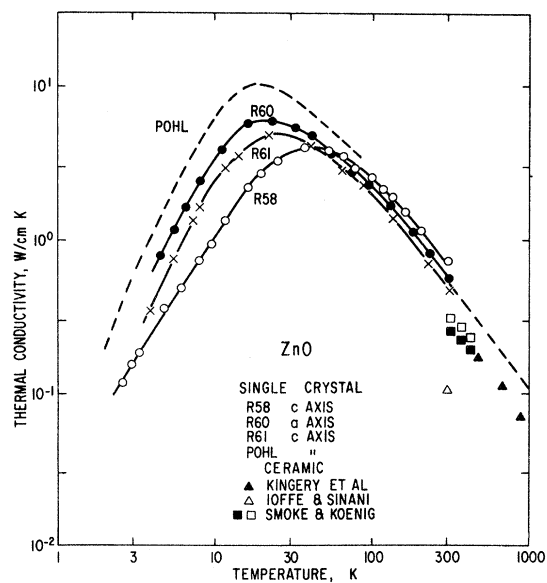


FIG. 1. Experimental values for the thermal conductivity vs temperature for single crystal and ceramic ZnO. The dashed curve below 100 K gives some results of Pohl (Ref. 6). The dashed curve above 300 K is a reasonable extrapolation of the present results.

TABLE I. Single-crystal samples studied.

Material	Sample No. ^a	Type ^b	L (mm)	D (mm)	log ₁₀ x (Fe)	Fe	Impurity Content ^c	Source	Comments
							Others		
ZnO hexagonal	R58	S	5.8	0.6	-5.0	0.4	Cu=0.5, Ti<0.7, φ≤1	G. Heiland, Erlangen, Germany	c-axis rod, colorless
	R60	S	3.2	1.6	<-5.2	<0.3	Cu<0.5, Ti<0.7, φ≤1	N. J. Zinc Co., New York, N. Y.	a-axis rod, colorless
	R61	S	3.4	1.9	<-5.2	<0.3	Cu<0.05, Ti<0.7, φ≤1	N. J. Zinc Co., New York, N. Y.	c-axis rod, colorless
	Pohl	S	>3	0.75	?	?	?	Minnesota Mining & Mfg., Minneapolis, Minn.	c-axis, rod, 30 Ω cm at 300 K, colorless
ZnS hexagonal	R116	S	12.7	2.6	<-5.0	<0.2	Al=0.5, Cu=0.3, Ni=0.4, Si<0.4, φ≤0.2	Eagle Picher, Miami, Okla.	c-axis rod, melt grown, colorless
	R119	S	12.2	3.1	-5.0	0.2	Al=7, Si=9, φ≤0.3	W. Piper, GE R&DC	c-axis rod, vapor grown, colorless
	R130	S	11.0	2.2	-5.8	0.03	Al=0.02, C=0.3, N=0.2, O=1.4, φ≤0.04	M. Aven, GE R&DC	Vapor grown, lemon-yellow color
ZnSe cubic	R164	S	11.7	3.2	-4.6	0.6	Cd=1.1, Cr=2.0, Mn=0.6, φ≤0.5	Eagle Picher, Miami, Okla.	Melt grown, reddish-yellow color
	R91	S	4.3	0.5	-4.7	0.3	Al=0.6, Si=0.6, φ≤0.1	M. Aven, GE R&DC	Vapor grown, red-brown color, 10 Ω cm
CdTe cubic	R96	S	9.0	2.4	<-5.4	<0.06	Li≤1, Zn≤0.5, φ≤0.4	M. R. Lorentz, GE R&DC	Melt grown, opaque, metallic luster
	R127	S	8.6	2.9	-5.2	0.10	φ≤1	H. D. Coghil, GE R&DC	Melt grown, opaque, metallic luster
	R93	S	11.0	2.8	-5.0	0.1	Si=0.4, φ≤0.2	M. R. Lorentz, GE R&DC	Melt grown, opaque, metallic luster
	R121	S	13.8	3.3	-2.9	17.0	φ≤5	S. Galginaitis, GE R&DC	Melt grown, opaque, metallic luster
	R123	S	12.8	4.1	-2.9	17.0	φ≤5	S. Galginaitis, GE R&DC	Melt grown, opaque, metallic luster
	R170	S	20.0	4.6	-1.9	170.0	Mg=2, Si=5, φ≤1	S. Galginaitis, GE R&DC	Melt grown, opaque, metallic luster
	R133	S	3.5	1.3	-5.3	0.1	Cd≤0.2, φ≤0.2	J. S. Prener, GE R&DC	Vapor grown in HCl gas, colorless
ZnS cubic	R139	N	6.1	2.0	-4.0	2.6	Cd=90, Cu=2, Mn=5, Si=4, φ≤1	Franklin, New Jersey	Light yellow color, some precipitate phase
	R118	N	16.3	4.7	-2.8	41.0	Cd=10, Cu=2, φ≤0.2	Santander, Spain	Medium yellow-brown color
	R114	N	10.4	2.9	-2.7	49.0	Cd=110, φ≤1	Summit County, Colo.	Yellowish-green color
	R117	N	14.1	4.6	-2.4	92.0	Cd=110, Cu=4, φ≤0.5	Baxter Springs, Kan.	Reddish-yellow color
	R140	N	9.6	2.4	-1.9	350.0	Cd=45, Co=3, Mn=9, φ≤1	Shiraita, Echigo, Japan	Dark yellow-brown color
	R115	N	10.5	3.4	-1.0	2700.0	Cd=0, Mn=9, Si=20, φ≤5	Balmont, New York	Opaque, black, dull
	R141	N	8.1	2.2	-0.75	4600.0	Al=8, Cd=80, Cu=6, Mn=180, φ≤1	Trepka, Yugoslavia	Opaque black, reddish-brown when thin

^aThe sample number refers to the sequential experimental run number in which the thermal conductivity was measured.

^bType S is synthetic single crystal; N is natural single crystal.

^cThe impurity concentration is given in units of 10¹⁸ atoms/cm³. The symbol φ stands for any other possible metallic impurity not listed.

IV. EXPERIMENTAL RESULTS

A. II-VI Compounds in General

The κ -vs- T curves for ZnO crystals are plotted in Fig. 1. Note that the present results are in reasonable agreement with those of Pohl⁶ and are somewhat higher than the earlier data²⁻⁴ on polycrystalline ZnO. A comparison of samples R60 and R61, which were from the same source with the same impurity content, shows that the thermal conductivity along the a axis, κ_a , is greater than that along the c axis, κ_c . The ratio $\kappa_a/\kappa_c \approx 1.2$ from 30 to 300 K. This result is in agreement with the observation of Jannettaz⁴ who stated that $\kappa_a/\kappa_c > 1$ by a noticeable amount. In contrast to this Martin and Wolf⁵ did not observe any significant anisotropy. The average thermal conductivity for ZnO, defined as $\frac{1}{3}(2\kappa_a + \kappa_c)$ is given as a function of temperature in Table II (see also Fig. 5).

The thermal conductivity of undoped ZnS has been measured on samples R116, R119, and R133. These results together with some values for natural cubic ZnS from the literature are shown in Fig. 2. These results show that the thermal conductivity of the hexagonal ZnS is much less than that of the cubic ZnS. In the 2–10 K range the thermal conductivity of the two hexagonal crystals is about 1% of the value imposed by boundary scattering at the walls of the crystal. After the data in Fig. 3 were taken, crystal R116 was heat treated in a liquid-zinc bath at 850 °C for 16 h, and crystal R119 was treated in sulfur vapor at 750 °C for 40 h. Both crystals were remeasured without any change ($\leq 10\%$) in their thermal conductivities. The low values of the phonon mean free path, which is calculated from the observed κ to be 6×10^{-3} and

TABLE II. Thermal conductivity values for II-VI compounds as a function of temperature.

Temp. (K) ^a	ZnO ^b R60 & R61	ZnS ^c R133	ZnSe ^c R130	ZnTe ^c R91	CdTe ^c R96
30	5.3	3.6	3.7	3.0	1.80
40	4.5	3.1	2.9	2.4	1.17
50	3.9	2.6	2.2	1.9	0.84
65	3.1	2.0	1.50	1.40	0.57
80	2.6	1.55	1.03	1.08	0.44
100	2.10	1.20	0.76	0.80	0.31
150	1.34	0.70	0.44	0.46	0.184
200	0.95	0.47	0.30	0.31	0.127
250	0.72	0.34	0.23	0.23	0.095
300	0.54	0.27	0.19	0.18	0.075

^aNo values are given below 30 K because such values depend on the size of the sample.

^bThe average thermal conductivity values for ZnO are computed from $\frac{1}{3}(2\kappa_a + \kappa_c)$, where κ_a and κ_c are taken from the a -axis and c -axis curves in Fig. 1.

^cThe thermal conductivity is given for the particular crystal as measured.

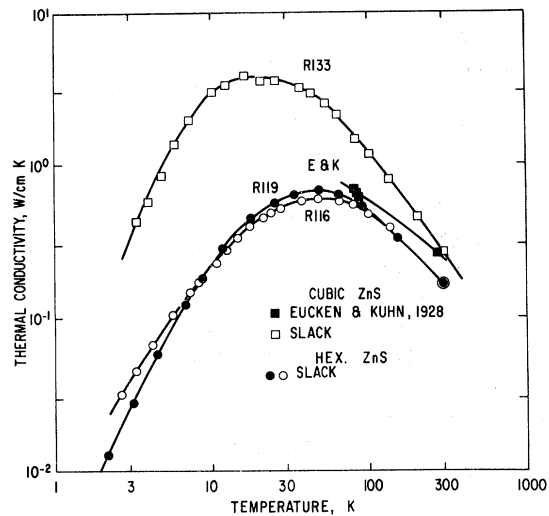


FIG. 2. Experimental values for the thermal conductivity vs temperature of pure synthetic crystals of cubic and hexagonal ZnS. The results of Eucken and Kuhn (Ref. 7) are for impure, natural crystals of cubic ZnS.

3×10^{-3} cm at 20 K for R116 and R119, respectively, is probably caused by stacking faults. Such faults are quite common in hexagonal ZnS.⁵⁶ A microscopic observation of R116 and R119 under crossed polarizers revealed that the average width of a birefringence band was 1.3×10^{-3} cm in R116 and 0.6×10^{-3} cm in R119. These distances show that at 2 K a phonon traverses about five bands before being scattered. It is clear that "hexagonal"

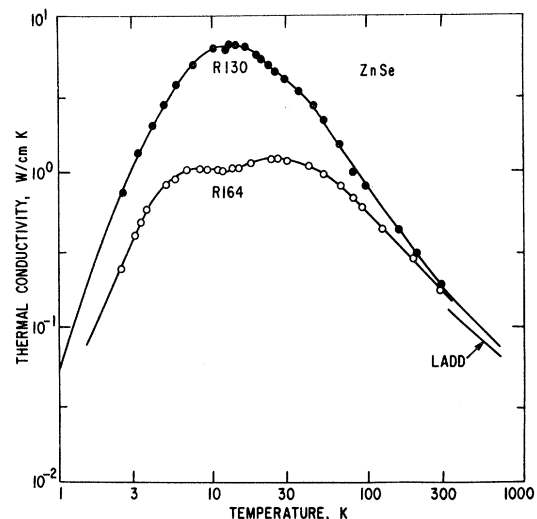


FIG. 3. Experimental values for the thermal conductivity vs temperature for two crystals of ZnSe. The results of Ladd (Ref. 8) are for polycrystalline ZnSe.

ZnS crystals currently available, even though quite pure chemically, have thermal conductivity values much lower than intrinsic ZnS. The synthetic cubic ZnS sample R133 is much better and has a much higher κ , though it is not yet exhibiting an intrinsic κ . This point will be returned to later.

The results for the two ZnSe samples R130 and R164 are shown in Fig. 3. Sample R130 is nominally pure and contains a trace of Fe, while R164 contains Cr and Fe. The results of Ladd⁸ on polycrystalline ZnSe are also shown. In Fig. 4 sample R91 of ZnTe is compared with the results of Kelemen *et al.*¹⁰⁻¹²

In Fig. 5 the κ -vs- T curves for all four Zn compounds have been plotted together. The respective κ values have been plotted reduced by successive factors of 10 to avoid overlap. All of the curves have very nearly the same shape. The κ maximum shifts to slightly lower temperatures in the series ZnO, ZnS, ZnSe, ZnTe while the absolute value of κ between 30 and 300 K also decreases in this series.

It is instructive to intercompare all of the available data on II-VI compounds in a manner similar to that used by Steigmeier⁵⁷ for III-V compounds. In all of the adamantine structure II-VI compounds, except for HgSe and HgTe, the heat is carried by phonons at 300 K and the κ is determined by phonon-phonon scattering in the pure crystals. In this case the value of κ is given⁵⁷⁻⁵⁹ by

$$\kappa = b\bar{M}\delta\Theta^3, \quad (2)$$

where b is a constant, \bar{M} is the average atomic mass in grams, δ^3 is the average volume occupied

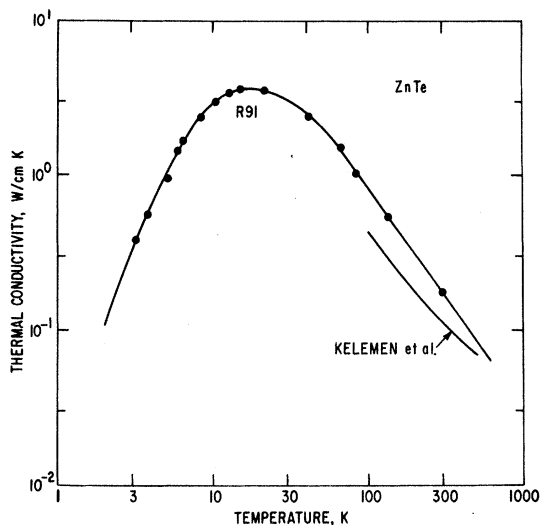


FIG. 4. Experimental values for the thermal conductivity vs temperature for ZnTe compared to the results of Kelemen *et al.* (Refs. 10-12).

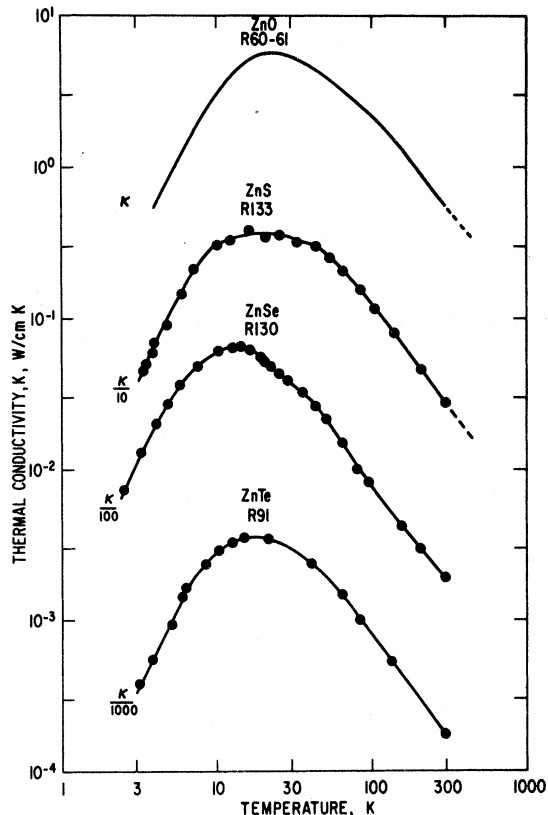


FIG. 5. Experimental values for the thermal conductivity κ vs temperature for nominally pure single crystals of ZnO, ZnS, ZnSe, and ZnTe. The curve for hexagonal ZnO is an average of the results for the two different crystal axes κ_a and κ_c . The results on successive crystals have been plotted reduced in κ by successive factors of 10 in order to avoid overlapping curves.

by one atom of the crystal, and Θ is the Debye temperature extrapolated to absolute zero. If the Grüneisen parameter γ is assumed to be equal to 2, the theoretical value^{58,59} of b is $b = 4.8 \times 10^{-3}$ W/g cm² K⁴ at 300 K. In Table III the values of Θ for the various elements and compounds have been collected from the literature.^{1,21,60-71} The values of κ at 300 K have also been taken from the available literature,^{1,10,12-21,29-32,57,72-74} as well as the present measurements. Data for the elements Si and Ge as well as the two III-V compounds GaAs and InSb are included in Table III. These two compounds have nearly equal atomic masses. In Fig. 6 the measured κ at 300 K is plotted versus the scaling parameter $\bar{M}\delta\Theta^3$. A straight line on this log-log plot fits the data fairly well except for HgSe and HgTe. The experimental value of b ranges from 4.9×10^{-3} W/g cm² K⁴ for CdTe to 7.4×10^{-3} W/g cm² K⁴ for BeO. Hence b varies from the theoretical value at CdTe to 1.5 times this value at BeO. The absolute magnitude of κ

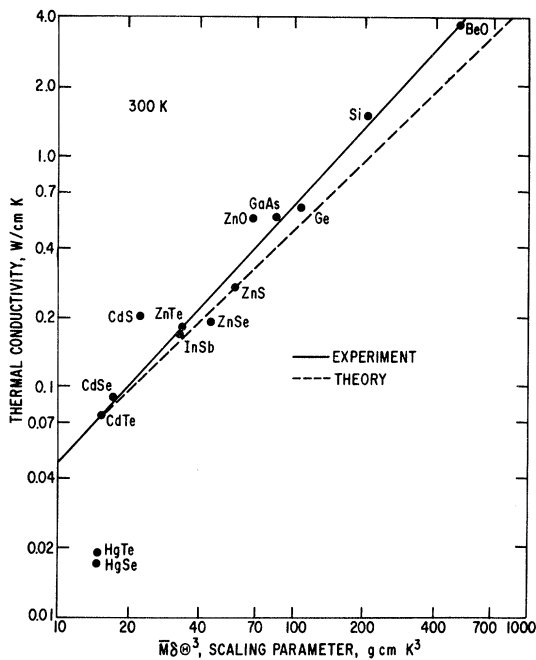


FIG. 6. Thermal conductivity at 300 K of II-VI and other adamantine compounds as a function of the scaling parameter $\bar{M}\delta^3$, see Eq. (2). The dashed line shows the theoretical prediction if $\gamma=2$. The solid line is the best experimental fit.

is in good agreement with the theory for these II-VI compounds as well as for Si, Ge, GaAs, and InSb. The only exceptions are HgSe and HgTe which have a κ of only 25% of that which would be expected. It is possible that the Θ values⁶⁵⁻⁶⁷ for HgSe and HgTe are in error. An earlier report⁷⁵ gave $\Theta = 105$ K for HgTe. Steigmeier⁷⁶ has shown that for III-V compounds the value of Θ varies as

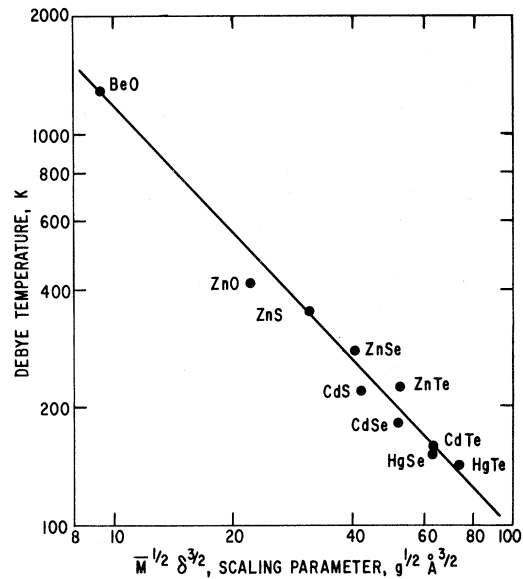


FIG. 7. Debye temperature of II-VI compounds vs the scaling parameter $\bar{M}^{1/2}\delta^{3/2}$, see Eq. (3).

$$\Theta = d(\bar{M}\delta^3)^{-1/2}, \quad (3)$$

where d is some constant. Hence in Fig. 7 the value of Θ given in Table III is plotted versus $(\bar{M}\delta^3)^{1/2}$. The straight line shown in Fig. 7 fits all of the data points fairly well, and shows that the Θ values in Table III are nearly correct, particularly those for HgSe and HgTe. Hence the especially low κ values for those two compounds in Fig. 6 are probably a real effect. This same property of HgSe and HgTe has been noted before by Kelemen *et al.*,^{10,12} and was attributed to an especially strong scattering of acoustic phonons by interaction with

TABLE III. Thermal conductivity at 300 K and the scaling parameter $\bar{M}\delta^3$ for various crystals.

Crystal	\bar{M} (g)	δ (10^{-8} cm)	Θ (K)	$\bar{M}\delta^3$	κ (W/cm K)	Reference Θ	κ
BeO	12.51	1.904	1280	500.	3.7	1, 60	1
ZnO	40.68	2.283	416	66.9	0.54	60, 61	a
ZnS	48.72	2.704	350	56.5	0.27	60, 62	a
ZnSe	72.16	2.834	279	44.4	0.19	63	a
ZnTe	96.48	3.045	225	33.5	0.18	63	a
CdS	72.23	2.923	219	22.2	0.20	60, 64	13-18
CdSe	95.68	3.039	181	17.2	~ 0.09	60	19 ^b
CdTe	120.00	3.240	158	15.3	0.075	21, 60, 65	13, 21
HgSe	139.78	3.042	151	14.6	0.017	66	29-32
HgTe	164.10	3.215	141	14.8	0.019	65, 67	10-12
Si	28.09	2.715	645	205.	1.56	68	72
Ge	72.59	2.829	374	107.4	0.60	68	72
GaAs	72.32	2.827	345	84.0	0.55	69, 70	73
InSb	118.28	3.239	205	33.0	0.17	70, 71	57, 74

^aPresent work.

^bEstimate, extrapolated from 100 K.

optical-branch phonons. More work is needed before this suggestion is accepted. Of particular importance would be an intercomparison of the phonon dispersion curves of HgSe and HgTe⁶⁵ with those of other II-VI compounds. It is also possible that κ is low because of phonon scattering from lattice vacancies or interstitials, since these two compounds are very difficult to make at the stoichiometric composition.

So, aside from HgSe and HgTe, the magnitude of κ at 300 K for all of the II-VI compounds is reasonable. The largest deviation from the straight line in Fig. 6 occurs for CdS and ZnO. An explanation for this deviation might be found in the fact that these two compounds have rather large cation-to-anion mass ratios (3.5 and 4.1).

B. Iron-Doped Crystals

The present study shows the effects of Fe²⁺ impurities on the κ of ZnS and CdTe. From a knowl-

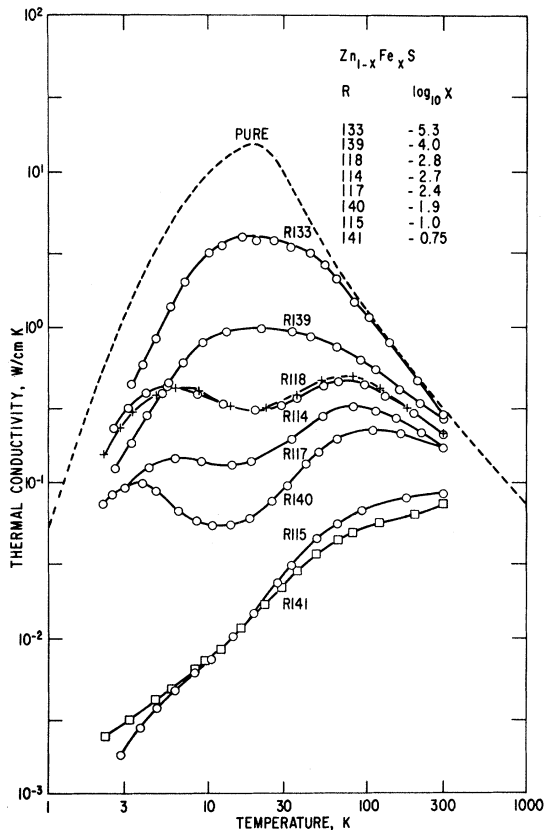


FIG. 8. Experimental values for the thermal conductivity vs temperature of single crystals of cubic ZnS containing various concentrations of Fe. All except R133 are natural crystals. The parameter x gives the mole fraction of substitutionally incorporated FeS. The dashed curve labeled PURE has been estimated by assuming $x = 0$.

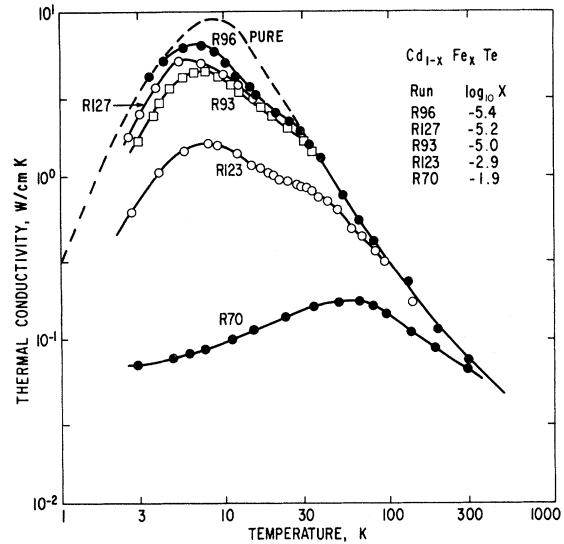


FIG. 9. Experimental values for the thermal conductivity vs temperature of synthetic single crystals of CdTe containing Fe. The parameter x gives the mole fraction of FeS. The dashed curve labeled PURE has been estimated by assuming $x = 0$.

edge of the κ -vs- T behavior of the undoped II-VI compounds the curves for $x = 0$ in Figs. 8 and 9 have been estimated. Note that the κ of both ZnS and CdTe is very sensitive to small traces of Fe²⁺. A concentration of 3 ppm of Fe decreases κ at 20 K by a factor of at least 2 for both crystals. The phonon scattering cross section is quite large. Since such small traces of Fe are difficult to avoid or eliminate, particularly in natural crystals, the intrinsic κ has to be estimated for pure ZnS.

In Fig. 8 for ZnS the large range of κ values is particularly noteworthy. Increasing amounts of Fe decrease κ very markedly. Samples R118 through R141 show a dip in the κ -vs- T curve in the 10–30 K range. This dip, centered at ~ 20 K, is related to the equivalent temperature $T_E = 21.6$ K for Fe in ZnS. The main tasks of the theory are to explain the large scattering cross section of Fe and the observed temperature dependence. The general approach has been outlined by Slack and Galginitis²¹ (see Sec. V).

The results for the synthetic CdTe are shown in Fig. 9 for several different concentrations of Fe. Even with repeated zone refining it was not possible to reduce the Fe concentration below 4 ppm ($\log_{10} x = -5.4$) as in sample R96. Hence no experimental data are available for $x = 0$. In CdTe the dip in the κ -vs- T curve centers around 25 K, in agreement with $T_E = 26.8$ K. The dip is not as pronounced for CdTe as it is for ZnS. However, the same theory should apply to CdTe because the energy level structure of the Fe²⁺ ions is the same

as in ZnS.

The dip in the κ curve for doped ZnSe, sample R164, shown in Fig. 3 is probably caused by the presence of the Fe^{2+} impurity. Although there is some Cr^{2+} present in somewhat higher concentrations than the Fe^{2+} , the Cr^{2+} excited states⁷⁷ are fewer in number and occur at lower energies than those of Fe^{2+} . Hence we believe the resonance phonon scattering is produced by the Fe^{2+} . More work would be needed to clearly separate the effects of Cr^{2+} from those of Fe^{2+} impurities. The Mn^{2+} impurity can be neglected as a possible source of phonon scattering.²¹

V. THEORETICAL ANALYSIS

The normal modes of vibration of a tetrahedron have⁷⁸ the irreducible representations $A_1 + E + T_2$. The ground state of the Fe^{2+} ion is an orbital E state.⁵³ Since it is the orbit-lattice interaction²¹ that is responsible for scattering the phonons, then only those phonons that produce an E -mode distortion of the tetrahedron will be absorbed and reemitted (i. e., scattered) by the Fe^{2+} ions. This can be seen from the group multiplication table⁷⁹ for T_d point symmetry. The allowed one-phonon transitions for this case are given in Fig. 10(a). It is clear that only phonons of energy 2Δ will be scattered by this mechanism. It is, however, the strongest scattering produced by the Fe^{2+} ions.

Owing to the spin-orbit coupling there will be some admixture of the orbital T_2 wave functions (at energy $10Dq$ above the ground state) into the ground state. This admixture is given by the coefficients c_i of Eq. (A10) of Ref. 51, and is generally small. This admixture will permit scattering of those phonons which produce a T_2 distortion of the tetrahedron. The allowed one-phonon transitions for this much weaker process are shown in Fig. 10(b). Note that phonons of energy 1Δ , 2Δ , and 3Δ can now be scattered. The important feature of Fig. 10 is that there are no allowed transitions of energy 1Δ starting from the ground state. However, such 1Δ transitions can occur when the Γ_4 level becomes thermally populated at about 25

K. It is this sudden onset of the thermal population of the Γ_4 level that is believed to be responsible for the dip in the κ -vs- T curve of these Fe^{2+} -doped crystals. Since the phonon scattering produced by the $\Gamma_4 \rightarrow \Gamma_3$ transition (Fig. 10) will depend on the population difference²¹ between these two levels, the scattering will die away again at high temperatures. Hence the κ at high temperatures of the Fe^{2+} -doped crystals is close to that of the undoped ones.

An accurate theory of the phonon scattering by the Fe^{2+} will give the actual strengths of the allowed transitions shown in Fig. 10 as well as their dependences on the population differences between the levels. The strengths will depend on the wave functions of the individual levels.⁵³ This calculation is too lengthy for the present paper.

VI. CONCLUSIONS

(i) Measurements of the thermal conductivity κ of the II-VI compounds ZnO, ZnS, ZnSe, ZnTe, and CdTe have been made from 3 to 300 K. The behavior of all of the undoped compounds is similar. The κ at fixed temperature decreases in the series as listed.

(ii) The κ at 300 K for all of the adamantine structure II-VI compounds as well as Si, Ge, GaAs, and InSb can be related to the scaling parameter $\bar{M}\delta\Theta^3$. Only HgSe and HgTe appear to deviate substantially from this curve; their κ values are too low by a factor of about 4.

(iii) The κ of Fe^{2+} -doped samples of ZnS and CdTe show substantial depressions in the 5–50 K temperature range. This is caused by resonant phonon scattering from the five low-lying levels of the Fe^{2+} ions. These levels are equally spaced in energy by an amount Δ . A calculation of the allowed one-phonon transitions by the use of group theory shows that only 1Δ , 2Δ , and 3Δ transitions are permitted. The 2Δ transitions are believed to be by far the strongest.

(iv) So-called hexagonal ZnS crystals appear to have very low κ values caused by phonon scattering from stacking faults. The crystals are really not perfectly hexagonal.

(v) The anisotropy in κ of ZnO is small. From 30 to 300 K the ratio κ_a/κ_c is about 1.2.

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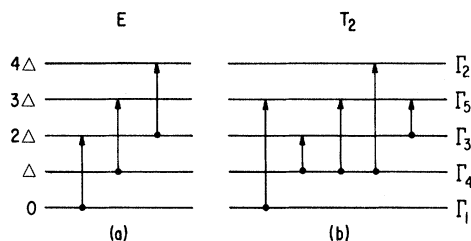


FIG. 10. Allowed one-phonon-absorption transitions for phonons producing (a) E -mode distortions of the tetrahedron and (b) T_2 -mode distortions.

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Frequency- and Wave-Vector-Dependent Dielectric Function for Ge, GaAs, and ZnSe †

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The frequency- and wave-vector-dependent dielectric function for Ge, GaAs, and ZnSe is calculated from the electronic band structures obtained by the empirical-pseudopotential method. The results show the effect of increasing ionicity on the dielectric function. The results also yield the plasmon dispersion relation $\omega(q)$ for the three semiconductors. The frequency- and wave-vector-dependent Penn dielectric function is calculated and compared with the results for Ge.

I. INTRODUCTION

We have calculated¹ the frequency- and wave-vector-dependent dielectric function $\epsilon(\vec{q}, \omega)$ in the [100] direction for Ge, GaAs, and ZnSe. This dielectric function describes the screening of a longitudinal field which varies in both space and time. This is the first calculation of $\epsilon(\vec{q}, \omega)$ for these materials using realistic energy bands and wave functions. These three crystals were chosen to observe the changes in $\epsilon(\vec{q}, \omega)$ as one moves through a series from a completely covalent compound (Ge) to compounds with decreasing covalency (GaAs and ZnSe).

The present calculations of $\epsilon(\vec{q}, \omega)$ are similar to that done by Walter and Cohen² for Si. The real part of the dielectric function, $\epsilon_1(\vec{q}, \omega)$, is calculated directly, and the imaginary part, $\epsilon_2(\vec{q}, \omega)$, is calculated using the Kramers-Kronig transforma-

tion. The details and results of the calculation are given in Sec. II. In Sec. III the results for Ge are compared with a calculation of $\epsilon_1(\vec{q}, \omega)$ using the Penn model.³

II. CALCULATIONS AND RESULTS

First we calculate the longitudinal-wave-vector- and frequency-dependent dielectric function $\epsilon(\vec{q}, \omega)$ which describes the crystal response to an electric field parallel to \vec{q} and varying sinusoidally in time:

$$\vec{D} e^{i(\vec{q} \cdot \vec{r} - \omega t)} = \epsilon(\vec{q}, \omega) \vec{E} e^{i(\vec{q} \cdot \vec{r} - \omega t)}. \quad (2.1)$$

Using the result for ϵ_1 obtained by Ehrenreich and Cohen,⁴ we obtain

$$\epsilon_1(\vec{q}, \omega) = 1 + \frac{4\pi e^2}{\Omega q^2} \sum_{\vec{k}, c, v} |\langle \vec{k}, c | \vec{k} + \vec{q}, v \rangle|^2 \times \{ [E_c(\vec{k}) - E_v(\vec{k} + \vec{q}) - \hbar\omega]^{-1}$$