Resonant scattering of phonons by iron impurities in zinc sulphide

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A phenomenological model has been proposed for the resonant scattering of phonons due to magnetic impurities. The expression for the defect relaxation rate, which also includes Rayleigh scattering of phonons, is of the form

$$\tau_{\text{defect}}^{-1} = A_{\text{defect}}\ \omega^4 + \sum_i\ H_i\ \frac{\omega}{(\omega - \omega_{0i})^2}\ F_i(T),$$

where A_{defect} is the Rayleigh scattering strength; i ($= 1,2,3,...$) denotes a particular phonon-induced electronic transition; H_i represents the strength of spin-phonon coupling; and $F_i(T)$ is the fractional electron population difference between the levels involved in the ith electronic transition. The model has been applied to explain resonance structure of K vs T curves of iron-doped ZnS. The success of the model lies in the fact that it gives consistently excellent agreement between theory and experiment for lightly as well as for heavily doped specimens. The model is, however, a simplification and does not consider, among other concepts, phonon dispersion, phonon polarization, phonon normal process, and phonon scattering by Raman processes.

I. INTRODUCTION

In recent years the technique of low-temperature thermal-conductivity measurements has been used increasingly as a means for studying the interactions between phonons and lattice defects. Particular interest has been focused on defect systems which display a resonant interaction with phonons. These resonances manifest themselves as dips in plots of thermal conductivity versus temperature. The dips are pronounced over relatively narrow ranges of temperature and correspond to strong scattering of phonons over a relatively narrow range of phonon frequencies.

In the present paper we wish to consider resonances, due to Fe^{2+} ions in ZnS, which have been observed by Slack[1] during thermal-conductivity measurements of II-VI compounds, pure and doped. A number of previous studies of thermal-conductivity measurements[2-13] have shown that Fe ions can drastically lower the thermal conductivity of crystals of Ge,[3] $ZnSO_4 \cdot 7H_2O$,[4] $CdTe$,[2,8] $MgCr_2O_4$,[5] $MgAl_2O_4$,[6,7] ZnS,[8] $KZnF_3$,[9] and MgO.[10-13] In these crystals the Fe^{2+} ions have either tetrahedral[2,5-8] or nearly octahedral[4,9-13] coordination with their nearest neighbors. The interaction of the phonons with the Fe^{2+} ions appears to be strong for both types of coordinations. In ZnS, Fe^{2+} ions have tetrahedral coordination in which phonon interaction is believed to take place[2] by means of phonon absorption, which produces upward transitions between low-lying energy levels of the d-shell electrons of the isolated Fe^{2+} ions. A resonant scattering occurs when the phonon energy is equal to the interlevel spacing.

The existence of a total of five low-lying energy levels has been determined for tetrahedral Fe^{2+} ions in ZnS[14-18] by optical techniques in the near and far infrared. To a first approximation, all the levels are equally spaced by an amount Δ ($= 15$ cm^{-1}). This opens the possibility of resonant scattering of phonons of energy 1Δ, 2Δ, 3Δ, and 4Δ. The group-theoretical studies of allowed one-phonon transitions, however, show that only 1Δ, 2Δ, and 3Δ transitions are permitted for mixed E and T_2 distortion (see Fig. 10 of Ref. 1). However, 1Δ transitions between Γ_1 and Γ_4 are found to be operative in highly doped and strained specimens such as $R140$ and $R115$. In this paper, we develop a simple model for this resonant scattering which explains the temperature and Fe-concentration dependence of thermal conductivity. This theory employs a simple Debye model for lattice phonons, uses Boltzmann statistics for the electron populations of the d-shell levels, and has two phenomenological parameters: H_i, the spin-phonon coupling parameter; and S^2, related to effective number of Fe^{2+} ions acting as a point defect in the lattice.

The frequency- and temperature-dependence of the resonance relaxation rate has been described by

$$\tau_i^{-1} = \sum_i H_i\ \frac{\omega}{(\omega - \omega_{0i})^2}\ F_i(T)\ ,$$

where i denotes a particular phonon-induced electronic transition, H_i represents the strength of the spin-phonon coupling, and $F_i(T)$ is the fractional electron-population difference between the levels involved in the ith electronic transition. Besides resonance scattering, iron impurities also cause Rayleigh scattering of phonons, which is produced

by the local mass difference, and lattice distortion, caused by substituting an Fe^{2+} ion for a Zn^{2+} ion. The effective relaxation rate, due solely to iron impurities, is expressed as

$$\tau^{-1}_{\text{defect}} = A_{\text{defect}}\omega^4 + \sum_i H_i \frac{\omega}{(\omega - \omega_{0i})^2} F_i(T) ,$$

where A_{defect} is the Rayleigh scattering strength, characteristic of added impurities.

The success of the model, which incorporates the above relaxation rate for the defect scattering, lies in the fact that it gives excellent agreement between theory and experiment in the case of lightly as well as heavily doped specimens. The model does not consider, among other concepts, phonon dispersion, phonon polarization, phonon normal-processes, and phonon scattering by Raman processes. The normal (N) processes are neglected, since the purpose of the present treatment is less to get an exact parametric fit than to show that resonance scattering must play an important role. The fact that a fit was obtained consistently for pure and doped materials, without invoking N processes, implies that either N processes are weak, or that umklapp (U) processes are as strong as N processes when N processes are strong. The present treatment would break down in the case of resonance scattering when N processes are relatively strong but U processes are relatively weak. However, such cases of resonance scattering are very rare.

II. THEORY

The theory that is used to predict the lattice thermal conductivity $K(T)$ as a function of temperature is based on the formulations of Klemens[19] and Callaway.[20] It gives

$$K(T) = \frac{K_B}{2\pi^2 v}\left(\frac{K_B T}{\hbar}\right)^3$$

$$\times \int_0^{\Theta_D/T} \tau_c(x, T) \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad x = \frac{\hbar\omega}{K_B T} , \quad (1)$$

where Θ_D is the Debye temperature; v is the average sound velocity; T is the temperature; $\hbar$ and K_B are Planck's constant divided by 2π and Boltzmann's constants, respectively.

The most important parameter in this theory is the combined relaxation time for phonons, τ_c, which is assumed to be given by contributions from individual processes by the sum of the individual relaxation rates:

$$\tau_c^{-1} = \sum_j \tau_j^{-1} = \tau^{-1}_{\text{pure}} + \tau^{-1}_{\text{defect}} , \quad (2)$$

where τ^{-1}_{pure}, which in itself is a sum of terms, contains all the information describing the phonon scattering in the undoped crystals, and $\tau^{-1}_{\text{defect}}$ con-

tains the information concerning the phonon scattering by deliberately added impurities.

The general procedure adopted is to use Eq. (1) to find the proper $\tau^{-1}_{\text{pure}}(\omega, T)$, which gives the best fit to the thermal conductivity of the pure crystal. Then, without changing $\tau^{-1}_{\text{pure}}(\omega, T)$, a form for $\tau^{-1}_{\text{defect}}(\omega, T)$ is obtained to fit the doped-crystal data. The parameters and even the mathematical form of the $\tau^{-1}_{\text{defect}}(\omega, T)$ will reflect the characteristics of the model assumed for the impurity. Now we shall discuss separately the various scattering processes present in pure and doped crystals.

A. Pure crystal

Traditionally, four relaxation rates are used to characterize the pure crystal. They are due to boundary, point-defect, umklapp, and normal scattering of phonons. The combined relaxation rate for pure crystal is written

$$\tau^{-1}_{\text{pure}} = \tau^{-1}_{\text{bd}} + \tau^{-1}_{\text{pt}} + \tau^{-1}_U + \tau^{-1}_N . \quad (3a)$$

The various terms on right-hand side have well established forms. The relaxation rate for boundary scattering is given by

$$\tau^{-1}_{\text{bd}} = v/L = E_{\text{bd}} , \quad (3b)$$

where L is Casimir length and v is the velocity of sound. For crystals of square cross section of side d, $L = 1.12d$; for crystals of noninfinite length, end corrections are necessary. However, for some reason, the value of τ^{-1}_{bd} that one calculates usually fails to reproduce the data at lowest temperature.

The relaxation rate for scattering by the natural isotopes in a pure crystal is given by

$$\tau^{-1}_{\text{pt}} = A\omega^4 = (3 V_0 \Gamma/\pi v^3)\omega^4 = E_{\text{pt}} x^4 T^4 , \quad (3c)$$

where V_0 is the average volume of a single atom in the crystal, Γ is a constant which depends upon the relative concentration of the different isotopes and the average atomic mass of the host lattice, and v is the velocity of sound. Thus E_{pt} is calculable from atomic parameters. However, even the purest crystal contains some residual background impurities, and these impurities also obey a law of the form of Eq. (3c), at least at low concentrations. The actual value of E_{pt} needed to reproduce the data, then, is usually three to five times greater than the natural isotope value.

The greater difficulties in fitting pure crystal data are encountered in the choice of a relaxation time for phonon-phonon scattering. In his original treatment, Callaway[20] used the following expressions for umklapp and normal phonon-phonon processes:

$$\tau^{-1}_U = B_1\omega^2 T^3 e^{-\Theta/bT} , \quad \tau^{-1}_N = B_2\omega^2 T^3 ,$$

where Θ is the Debye temperature and b is a con-

stant of the order of 2 or 3. These expressions were used successfully by Callaway to fit data for pure Ge and LiF. However, in the present study it has been found necessary to depart from this formalism and follow Slack and Galginaitis,[2] who used for umklapp scattering

$$\tau_U^{-1} = B\omega^2(T/\Theta_D)e^{-\Theta_D/bT}$$

$$= E_U x^2 T^3 e^{-\Theta_D/bT} \ . \qquad (3d)$$

We have completely neglected the normal phonon relaxation rate, as Eq. (3d) has been found sufficient to describe intrinsic phonon scattering in pure crystals and gives good agreement at high temperatures. E_{bd}, E_{pt}, and E_U are called boundary, point-defect, and umklapp scattering parameters, respectively.

In summary, the combined relaxation rate for the pure crystal in terms of $x = \hbar\omega/K_B T$ takes the form

$$\tau_{pure}^{-1} = E_{bd} + E_{pt}X^4 T^4 + E_U X^2 T^3 e^{-\Theta_D/bT} \ . \qquad (3e)$$

B. Doped crystal

The central part of our problem is the determination of an appropriate defect scattering relaxation time. For this purpose, further simplifying assumptions will also be made. It will be assumed that the Fe^{2+} ions scatter phonons by two independent processes. The first process is that of an inactive point defect which produces a Rayleigh scattering. The second process is termed an active one, because the defect has internal degrees of freedom. The phonon scattering here is strongly frequency selective, because the phonons cause transitions to, and between, internal excited states which lie at discrete energies above the ground
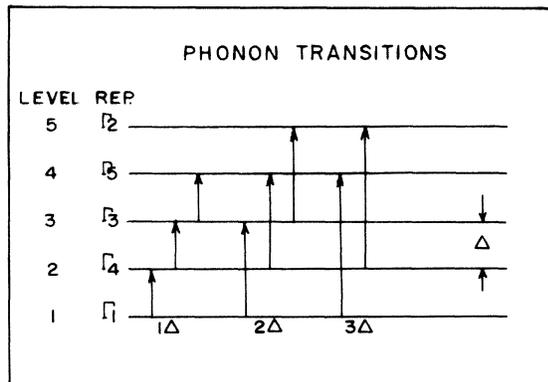
FIG. 1. Energy-level scheme for Fe, $3d^6$ impurities in ZnS showing the ground state and levels 2 through 5, all equally spaced by an energy $\Delta = 15.0 \ cm^{-1}$. The irreducible representations are given by the Γ_i. The allowed phonon-absorption transitions are given by solid arrows. Note that phonon absorption is possible for three different energies 1Δ, 2Δ, and 3Δ.
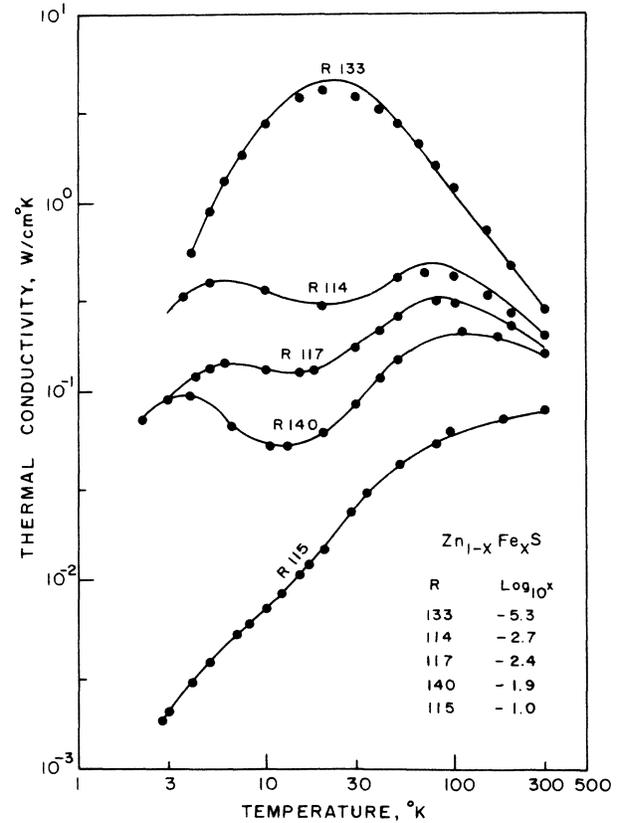
FIG. 2. Thermal conductivity versus temperature of single crystal of cubic ZnS containing various concentrations of Fe. Solid curves represent the theoretical results and circles the experimental results of Slack (Ref. 1). The parameter x gives the mole fraction of substitutionally incorporated FeS.

state. The Rayleigh scattering is produced by the local mass difference and the lattice distortion caused by substituting an Fe^{2+} ion for a Zn^{2+} ion. The relaxation rate for this type of scattering has the same frequency and temperature dependence as τ_{pt}^{-1}, and is given by[19,21]

$$\tau_i^{-1} = (3 V_0^2 N_T S^2/\pi v^3)\omega^4$$

$$= E_{pt}' x^4 T^4 N_T \ , \qquad (4a)$$

TABLE I. Parameters used for calculating the thermal conductivity of pure ZnS crystal.

Crystal diameter for R133 $L = 0.13$ cm
Average sound velocity $v = 3.13 \times 10^5$ cm/sec
Debye temperature $\Theta_D = 344$ °K
Average volume per atom $V_0 = 19.8 \times 10^{-24}$ cm^3
$\Gamma = 4.72 \times 10^{-5}$
$p = 5.10 \times 10^{-16}$ sec
$b = 3.0$
$K_B = 1.38 \times 10^{-16}$ erg °K^{-1}
$\hbar = 6.62 \times 10^{-27}$ erg sec
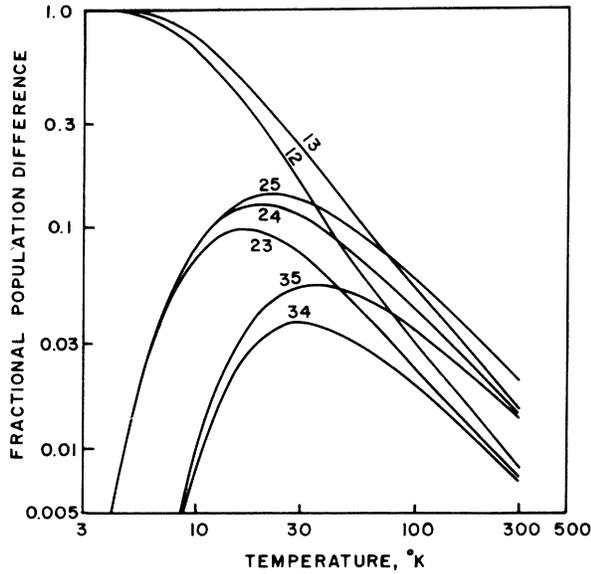
FIG. 3. Calculated population differences" between the electronic levels of the d-shell of Fe^{2+} ions in ZnS. The curves are labeled according to different transitions (e.g. 35 for $\Gamma_3 \rightarrow \Gamma_5$) shown in Fig. 1.

where N_T is the number of the Fe^{2+} ions per unit volume of the crystal, and S^2 is the total scattering number for the Fe^{2+} ions acting as a point defect in the lattice. The value of dimensionless parameters S^2 depends upon local difference in mass, lattice parameter, and interatomic bonding at the impurity site. Its values for various impurities in alkali halides has been estimated by Klemens,[21] and have been measured by Slack[22] and by Walker and Pohl.[23] The measured values range $2 \geq S^2 \geq 0$. In our case, an estimation of S^2 was not possible due to unavailability of data. However, the value $S^2 = 0.3$, found to give consistently excellent agreement for lightly as well as for heavily doped crystals, is similar to that for various impurities in alkali halides.

The second type of scattering is caused by the resonant scattering of Fe^{2+} ions from those phonons which have energies equal to one of the interlevel spacings Δ, 2Δ, 3Δ or 4Δ. This scattering is really an absorption and reemission of the phonons. The energy-level scheme for Fe^{2+} ions in ZnS is shown in Fig. 1. The allowed one-phonon transition permitted by group theory is also shown by solid arrows. This part of the problem has been treated phenomenologically, and we find that the following form of relaxation rate of phonons interacting resonantly gives excellent results:

$$\tau_r^{-1} = \sum_i H_i \frac{\omega}{(\omega - \omega_{0i})^2} F_i(T)$$

$$= \sum_i H_i \frac{x}{(x - x_{0i})^2} \frac{F_i(T)}{T}, \qquad (4b)$$

where $i (=1, 2, 3, \cdots)$ denotes a particular phonon-induced electron transition. The summation over i indicates that we are considering different transitions simultaneously. $\hbar\omega_{0i}$ represents the energy separation of the levels involved in the ith transition, and H_i is called the spin-phonon coupling parameter. $F_i(T)$ is the fractional electron-population difference between the levels involved in ith transition, and is calculable from Maxwell-Boltzmann statistics.

Thus, we can finally write τ_{defect}^{-1} in terms of $x = \hbar\omega/k_B T$ as

$$\tau_{defect}^{-1} = E_{pt} N_T x^4 T^4 + \sum_i H_i \frac{x}{(x - x_{0i})^2} \frac{F_i(T)}{T}. \qquad (4c)$$

We would like to emphasize at this point that the success of Eq. (4c) lies in the very fact that it gives excellent fits to the experimental results for lightly as well as for heavily doped crystals and, in turn, gives support to the various assumptions made in the theory.

III. RESULTS

The results of calculations using Eq. (1) together with Eqs. (3e) and (4c), respectively, for pure and

TABLE II. Parameters used for calculating thermal conductivity of doped crystals.

Crystal	$S^2 = 0.30$ Crystal diameter (cm)	Fe^{2+} conc. (atom/cm^3)	$\Delta = 15.0$ cm^{-1} E_{bd} (sec^{-1})	Spin-phonon coupling parameter H_i (sec^{-2})
R114	0.29	49×10^{18}	0.241×10^8	$H_{35} = 1.958 \times 10^{11}$
R117	0.46	92×10^{18}	0.30×10^8	$H_{24} = 5 \times 10^{10}$ $H_{25} = 1.5 \times 10^{11}$
R140	0.24	350×10^{18}	0.013×10^8	$H_{12} = 4 \times 10^8$ $H_{25} = 68.8 \times 10^{10}$
R115	0.34	2700×10^{18}	0.0092×10^8	$H_{12} = 2.407 \times 10^{10}$ $H_{25} = 1.30 \times 10^{12}$
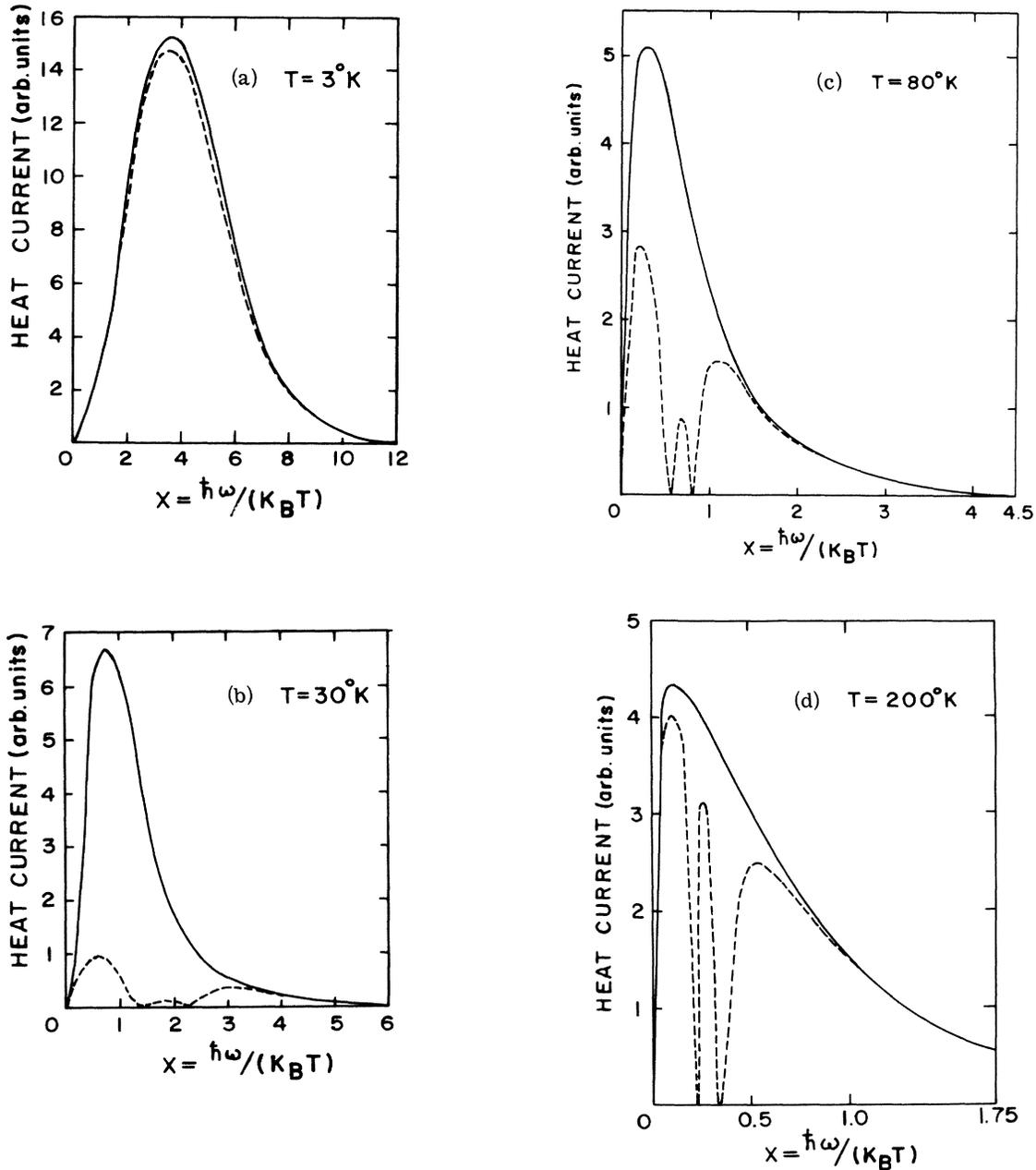
FIG. 4. (a)−(d) Calculated heat current for phonons of frequency ω plotted in arbitrary units as a function of $x = \hbar\omega/kT$ for four different temperatures ($T = 3$, 30, 80, and 200 °K). Solid line: Callaway model with no resonant scattering; dashed line: Callaway model with resonant scattering; $(N_T = 92 \times 10^{18} \text{ atom/cm}^3)$.

doped crystals are shown in Fig. 2, along with the experimental results of Slack.

First, the experimental data for undoped R 133 were fitted as best as possible. It was found necessary to depart from the theoretical value of E_{bd} to fit the low-temperature data; the value is given in Table I. The values of parameters p and b in the umklapp relaxation rate were found by matching the theoretical and experimental curves for T

> 100 °K. The value of E_{pt} used is about three times greater than the calculated value. Still, there are some deviations around the peak of the curve $R133$, and that might be due to some impurities present in $R133$.

To calculate thermal conductivity of doped crystals, we needed to know the energy-level scheme of Fe^{2+} ions in ZnS, and the various possible transitions between them. The five low-lying energy

levels of Fe^{2+} ions in ZnS are shown in Fig. 1; of these, two are singlet, two are triplet, and one is doublet. All levels are equally spaced in energy by $\Delta = 15$ cm^{-1}. Only 1Δ, 2Δ, and 3Δ transitions are permitted by group theory. For these transitions we have calculated the population difference factor $F_i(T)$ at different temperatures from Maxwell-Boltzmann statistics, and the results are shown in Fig. 3. The parameters used in calculations of thermal conductivity of crystals doped with different concentrations of impurities are given in Table II. Note that all the crystals, pure $R133$ and doped, have different sizes; proper changes in the boundary relaxation rate have been made accordingly.

For $R114$, only 2Δ transition $(3 \to 5)$ is sufficient to explain the data, except for slight deviations on the high-temperature side which can be removed if some higher-order transition is also considered. In all other cases, two transitions were found necessary and sufficient to explain experimental results. In the case of $R117$, we find that 2Δ $(2 \to 4)$ and $3\Delta(2 \to 5)$ transitions give excellent agreement, while for $R140$ and $R115$ we find it necessary to include a 1Δ transition starting from ground state with a 3Δ transition $(2 \to 5)$ for fitting the data.

Thus, with the inclusion of a Rayleigh scattering and a phenomenological resonance relaxation rate in the Callaway model, we have been able to consistently provide an explanation for K vs T data for lightly and as well as heavily doped crystals. It is worthwhile to note that the effect of the Rayleigh term is simply to reduce the conductivity in magnitude; it is only the resonant term which produces the desired waviness in the temperature dependence of the thermal conductivity. The effect of this resonant term can be illustrated very well with the help of Figs. 4(a)–4(d), where the contribution to the conductivity for phonons of frequency $\omega = xkT/\hbar$ is plotted against x for different temperatures. For each temperature, two curves are shown—one for $N_T = 92 \times 10^{18}$ atom/cm^3 and the other for $N_T = 0$—but the value of τ_i^{-1} [Eq. (4a)] has been included in both. Thus, the difference between the two curves is entirely due to the resonant term. The ratio of the conductivities with and without resonant scattering will equal the ratio of the areas under the curves. One can immediately make the following observations.

(i) At low temperature $(T = 3$ °K), spin-phonon coupling affects the conductivity to a very small extent. This is due to small values of $F_i(T)$, large values of x_{0i}'s at this temperature, and major contributions from boundary scattering.

(ii) At $T = 30$ °K, the effect of resonance scattering is very strong, so strong that the conductivity is reduced by a factor of 7. This is due to the fact that $F_i(T)$ has maxima in this temperature range and x_{0i}'s have small values.

(iii) At $T = 80$ °K, the intrinsic and resonant phonon scatterings are of the same order.

(iv) At $T = 200$ °K the effect of resonant scattering is again small, and conductivity is determined mainly by intrinsic phonon scatterings.

In summary, this analysis shows that the effect of resonance is strongest in the intermediate temperature range and is small on both the low- and the high-temperature sides. This result is characteristic of the model employed.

IV. CONCLUSION

We find that the observed conductivity can be accounted for very well with the help of a model of resonant scattering of phonons employing a simple Debye model for lattice phonons, Boltzmann statistics for the electron population of d-shell levels, and parameters S^2 related to Fe^{2+} impurities. The success of the model lies in the fact that it gives excellent agreement between theory and experiment for lightly as well as for heavily doped specimens. The theory is, however, a simplification, and it has neglected to consider, among other concepts, phonon dispersion, phonon polarization, phonon normal processes, and phonon scattering by Raman processes. The inclusion of such refinements might well alter the values found for the parameters given in Table II. However, we believe that such refinement will not affect our basic conclusion that Fe^{2+} ions in ZnS produce a resonant scattering of phonons.

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