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Phonon Conductivity of $CdTe:Fe^{+2}$ and $MgO:Fe^{+2}$

Neelmani and G. S. Verma
Department of Physics, Banaras Hindu University, Varanasi-5, India
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A phenomenological form for ω dependence of τ_r^{-1} is proposed which takes into account a term known as the population-difference factor. The thermal-conductivity-vs-temperature curves for $CdTe:Fe^{+2}$ and $MgO:Fe^{+2}$ are explained satisfactorily except that there are slight deviations at the low-temperature as well as at the high-temperature side.

I. INTRODUCTION

A number of studies of thermal-conductivity measurements, both at high and low temperatures, on semiconductors and insulators doped with impurities that are magnetic in nature (such as Fe, Mn, Co, etc.) have been reported by Slack and co-workers,[1–3] de Goer,[4] Morton and Lewis,[5] and Challis *et al.*[6] The general feature of the K-vs-T curves is that there are dips appearing in them, and the over-all conductivity is reduced considerably in comparison to those for the pure sample, with the reduction depending upon the concentration of impurities. A qualitative explanation for this suppression and the dips has been suggested by Slack[1] in terms of resonant scattering of phonons from the magnetic levels of these ions in the crystalline host.

The first quantitative analysis which employs the known energy levels of the excited states of the impurity ion (as deduced from far-infrared spectroscopy) has been given by Morton and Lewis.[5] The strength of the spin-phonon coupling has been deduced from spin-lattice relaxation-time measurements which identify an Orbach's process (i.e., in $MgO:Fe^{+2}$). The shape of the theoretical curve is more or less of the same form as the experimental one, whereas the thermal conductivity is heavily reduced at low temperatures. In fact, this reduction is due to the tail of the Lorentzian line-shape function in Eq. (13) of Ref. 5.

Far-infrared optical absorption of $CdTe:Fe^{+2}$ gives four peaks[7] at 18.6, 54.8, 66.7, and 73.2 cm^{-1} believed to be due to electronic transitions associated with the d-shell levels of Fe^{+2} ion impurities in tetrahedral lattice sites of CdTe. This indicates the possibility of four resonant-phonon-scattering processes that may take place from these levels, each having a different spin-phonon coupling.

Taking a level at 18.6 cm^{-1}, we tried to explain the curve R-87, with the corrected expression given by Morton and Lewis[5] [Eq. (13) of Ref. 5] for the relaxation rate of phonons due to resonant scattering from the magnetic levels as follows:

$$\tau_r^{-1}(x, T) = \alpha(1/T^3) f(x - x_0) F(x_0)(x/x_0^3), \qquad (1)$$

where $x = \hbar\omega/k_B T$, ω is the angular frequency of phonons in rad/sec, $x_0 = \hbar\omega_0/k_B T$, $\hbar\omega_0$ is the energy separation of the resonance level from the ground-state level, and α is an adjustable parameter. Further, $f(x - x_0)$ is the Lorentzian line-shape function and $F(x_0)$ is a population-difference factor derived from Maxwell-Boltzmann statistics. However, the theoretical calculations[8] were so discouraging that even when the simultaneous ef-

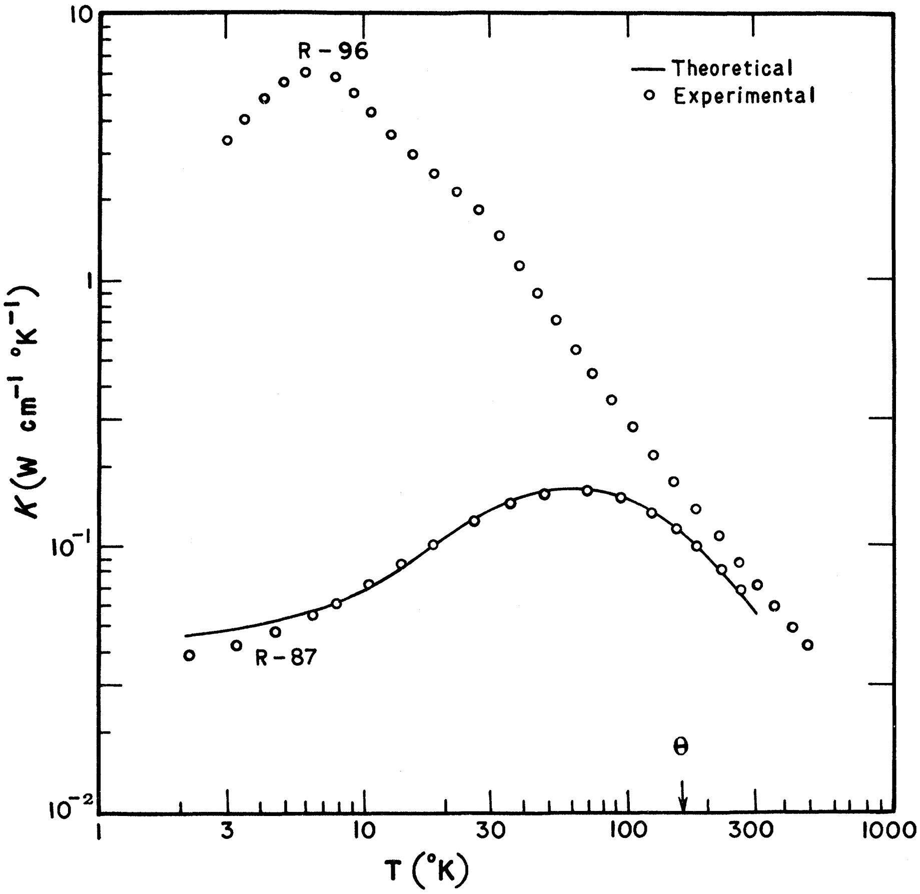

FIG. 1. Open circles R-96 and R-87 represent the experimental results of Slack and Galginaitis (Ref. 1) for the pure and doped CdTe samples, respectively. The iron-doping concentration is 1.6×10^{20} cm^{-3}. The solid curve represents the theoretical calculations for the doped sample.

fect of another level at 54.8 cm^{-1} was taken into account, the results could not be improved, and it then became necessary to seek some other form of ω dependence for τ_r^{-1}.

The phenomenological ω dependence for τ_r^{-1} in the form[9] $\tau_r^{-1}\propto\omega^4/(\omega_0^2-\omega^2)^2$ was tried at first, but the results were found to be in a bit larger disagreement with the experimental ones both at low and high temperatures. It has therefore been modified by including what is called the population-difference factor $F(\omega_0, T)$ derived from Maxwell-Boltzmann statistics. The modified expression for τ_r^{-1} is therefore

$$\tau_r^{-1}=C\,\frac{\omega^4}{(\omega_0^2-\omega^2)^2}F(\omega_0, T)\ . \qquad (2)$$

The form of this modification has been implied from the expressions of Morton and Lewis[5] for τ_r^{-1}.

With such a form for the ω dependence of τ_r^{-1}, it has been shown in the present paper that resonant scattering of phonons from only two levels at 18.6 and 54.8 cm^{-1} is sufficient to explain the observed thermal conductivities, except that there are slight deviations at the low-temperature side. Deviations on the low-temperature side are expected to be removed if proper changes in the point-defect scattering parameter are taken into account. In our calculations such a change, which is a must, has not been made because of the unavailability of data on changes in the force constants due to the presence of iron impurities in such a high concentration.

To support the inclusion of $F(\omega_0, T)$ in Eq. (2), some calculations on MgO:Fe^{+2} have been done also. It is found that the inclusion makes agreement with the experimental results somewhat improved, especially at the high-temperature side. The results are shown in the Fig. 2.

II. THEORY

The basis of the present study is Callaway's model which gives $K(T)$ as

$$K(T)=\frac{k_B}{2\pi^2 v}\left(\frac{k_B T}{\hbar}\right)^3\int_0^{\Theta/T}\tau_c\,\frac{x^4 e^x}{(e^x-1)^2}\,dx\ , \qquad (3)$$

where k_B is Boltzmann's constant, v is the average sound velocity, Θ is the Debye temperature, and

$$\tau_c^{-1}=\tau_b^{-1}+\tau_{pt}^{-1}+\tau_u^{-1}+\tau_n^{-1}+\tau_r^{-1}\ . \qquad (4)$$

The various relaxation rates on the right-hand side are due to the boundary, point-defect, Umklapp, normal, and resonant scattering of phonons,

TABLE I. Values of the parameter H_i ($i = 18.6$ and $54.8\ \text{cm}^{-1}$) at different temperatures used in the calculation of phonon conductivity of CdTe:Fe^{+2}. This involves the calculation of the factor $F(x_0)$ at different temperatures.

T (°K)	$H_{18.6}$ (sec^{-1})	$H_{54.8}$ (sec^{-1})
3.32	3.000×10^{10}	2.508×10^{7}
4.43	3.000×10^{10}	1.848×10^{8}
6.65	2.792×10^{10}	1.292×10^{9}
8.86	2.480×10^{10}	2.144×10^{9}
13.30	1.827×10^{10}	7.075×10^{9}
17.73	1.321×10^{10}	9.625×10^{9}
26.60	8.361×10^{9}	1.089×10^{10}
35.47	5.274×10^{9}	1.046×10^{10}
53.20	2.923×10^{9}	8.550×10^{9}
106.40	8.000×10^{8}	5.000×10^{9}
212.80	4.626×10^{8}	2.627×10^{9}

respectively. The success of Callaway's model in explaining K-vs-T curves for a pure CdTe sample, neglecting the normal processes, is evident from the comparison of the theoretical curve C with the experimental curve R-96 of Fig. 7 of Ref. 1. Moreover, it was not felt that Holland's model ($K = K_L + K_T$) taking separate contributions of longitudinal (K_L) and transverse phonons ($K_T = K_{T_1} + K_{T_2}$) was needed because of two reasons. First, because it's not definitely known whether the same expression for τ_r^{-1} will appear in the three thermal-conductivity integrals of K_L, K_{T_1}, and K_{T_2} or not. Second, in our case with a doping concentration of $1.6\times10^{20}\ \text{cm}^{-3}$, and where the conductivity is highly suppressed in the range 3–50 °K, the resonant-scattering term appears to be a highly effective one, and it is likely that such a minor modification will have a small effect in an explanation of curve R-87.

The various relaxation terms in Eq. (4) have the following calculable forms. The inverse relaxation time due to boundary scattering of phonons is $\tau_b^{-1} = v/L$, where v is the average phonon velocity

TABLE II. Values of the various constants used in the calculation of the phonon conductivity of CdTe:Fe^{+2}.

Crystal diameter (L) for sample R-96 = 0.24 cm
Crystal diameter (L) for sample R-87 = 0.29 cm
$k_B = 1.38\times10^{-16}$ erg °K^{-1}
$h = 6.62\times10^{-27}$ erg sec
Average sound velocity $v = 2.0\times10^{5}$ cm/sec
Debye temperature $\Theta = 160$ °K
Average volume per atom $V_0 = 34.04$ (Å)^3
Point-defect scattering parameter Γ (CdTe) = 2.31×10^{-5} sec^{-4}
$p = 6.28\times10^{-16}$ sec^{-1}
$b = 4.5$
$C = 3.0\times10^{10}$ sec^{-1}

TABLE III. Values of the parameter H_i ($i = 150\ \text{cm}^{-1}$) at different temperatures used in the calculation of phonon conductivity of MgO:Fe^{+2}.

T (°K)	H_{150} (sec^{-1})	$X_0 = 150/T$
10	1.0×10^{11}	15.00
20	1.0×10^{11}	7.50
30	1.0×10^{11}	5.00
40	1.0×10^{11}	3.75
50	8.80×10^{10}	3.00
60	8.07×10^{10}	2.50
80	6.80×10^{10}	1.88
100	5.64×10^{10}	1.50
150	3.91×10^{10}	1.00
200	3.00×10^{10}	0.75

and L is the characteristic length of the sample. The relaxation rate due to point-defect scattering of phonons τ_{pt}^{-1} is given by $\tau_{pt}^{-1} = D\omega^4$, where $D = 3V_0\Gamma/\pi v^3$, V_0 is the atomic volume, and Γ is the point-defect scattering parameter. The relaxation rate due to phonon-phonon Umklapp scattering is given by

$$\tau_r^{-1} = p\omega^2(T/\Theta)e^{-\Theta/bT} ,$$

where p is an adjustable parameter and Θ is the Debye temperature.

Since we are considering resonant scattering of phonons from only two levels, at 18.6 and 54.8 cm^{-1}, we have τ_r^{-1} given by Eq. (2) as

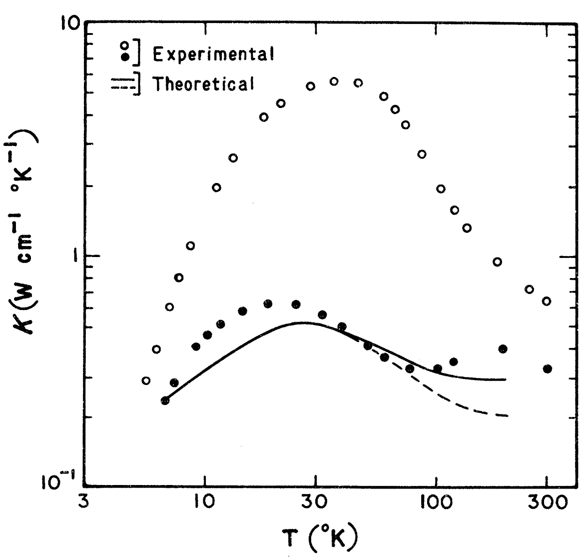

FIG. 2. Open and solid circles represent, respectively, the experimental results of Morton and Lewis (Ref. 5) for the pure and doped MgO samples. The iron-doping concentration is 7500 ppm. The solid and the dashed curves represent, respectively, the theoretical calculations when the factor $F(\omega_0, T)$ is taken into account and when it is not.

TABLE IV. Values of the various constants used in the calculation of phonon conductivity of MgO:Fe^{+2}. When the calculations are done without the factor $F(\omega_0, T)$ in Eq. (2), $C = 1.0\times 10^{11}$ sec^{-1}. When the factor $F(\omega_0, T)$ is taken as it is shown in Eq. (2), $C = 3.0\times 10^{11}$ sec^{-1}.

Mean molecular weight M	= 20.16 g
Density ρ	= 3.58 g cm^{-3}
Debye temperature Θ	= 760 °K
E_b	= 2.3×10^{7} sec^{-1}
E_u	= 0.05 sec^{-2} °K^{-5}
E_n	= 0.31 sec^{-1} °K^{-5}
E_{pt}	= 11.8 sec^{-1} °K^{-4}

$$\tau_r^{-1} = \sum_i H_i \frac{x^4}{(x_{0i}^2 - x^2)^2}, \tag{5}$$

where the parameter C and the population-difference factor $F(x_0)$ of Eq. (2) have been lumped into one parameter H_i known as the spin-phonon coupling-strength parameter. H_i is temperature dependent. This is, in fact, due to the temperature dependence of $F(x_0)$ itself. $\sum_i$ represents the simultaneous involvement of different transitions.

The basis of the study on MgO: Fe^{+2} has again been Callaway's model. The normal processes here need inclusion because they are found to make appreciable contributions, which is evident from the explanation of the K-vs-T curve for undoped MgO given by Morton and Lewis.[5] The combined relaxation rate for the doped MgO specimen is therefore given by

$$\tau_c^{-1}(x, T) = E_b + E_{pt} x^4 T^4 + E_u x^2 T^5 e^{-\Theta/2T} + E_n x T^5 + H_i [x^4/(x_{0i}^2 - x^2)^2] . \tag{6}$$

Here the resonant-phonon-scattering mechanism involves only the ground and the low-lying excited states of the Fe^{+2} ion in MgO that are separated by an energy corresponding to 150 °K. E_b, E_u, E_n, E_{pt}, and H_i are the various phonon-scattering parameters. The average sound velocity v in Eq. (3) is calculated with the help of the expression

$$v = \left(\frac{k_B \Theta}{\hbar}\right)\left(\frac{6\pi^2 N_0 \rho}{M}\right)^{-1/3},$$

where N_0 is Avogadro's number, M is the mean molecular weight, and ρ is the density.

III. RESULTS

The ω dependence of τ_r^{-1}, as it is in Eq. (1), is not able to explain the K-vs-T curve of CdTe : Fe^{+2}. A phenomenological ω dependence for τ_r^{-1} as is given in Eq. (2) has been tried and is found to give a satisfactory explanation for this behavior. The results of the calculations on CdTe : Fe^{+2} are shown in Fig. 1, as well as the experimental results of Slack.[1] The values of the different parameters used in the calculation of the phonon conductivity are given in Tables I and II.

As far as the effect of change of concentration on H_i is concerned, it appears from Fig. 2 of Ref. 1, contrary to the results reported by Morton and Lewis[5] and Challis *et al.*,[6] that with increase in the impurity concentration the conductivity is higher than it is at lower concentrations. Therefore, it appears that the concentration of 1.6×10^{20} cm^{-3} is some sort of a critical concentration, and thus this peculiar concentration dependence of H_i demands a thorough explanation.

The results of calculations on MgO: Fe^{+2}, with and without the factor $F(\omega_0, T)$, are shown in Fig. 2. A comparison with the experimental results of Morton and Lewis,[5] too, is shown. The results show better agreement when the factor $F(\omega_0, T)$ is included in the expression $\tau_r^{-1} \propto \omega^4/(\omega_0^2 - \omega^2)^2$. Therefore, this gives a better support to its inclusion in Eq. (2). The values of various constants and the adjustable parameters in Eq. (6) together with the other constants used in the calculation of phonon conductivity of MgO: Fe^{+2} are given in Tables III and IV. The Debye temperature Θ is assumed to have a constant value of 760 °K.

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