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PHONON RESONANT SCATTERING IN CdS CONTAINING Co^{2+}

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The thermal conductivity of CdS containing about 500 ppm of Co^{2+} has been measured from 0.35 to 4.0 K as a function of magnetic field for fields up to 20 kG. A typical conductivity dip appears in all curves. The position of the dip shifts to higher temperatures as the magnetic field increases. The results are qualitatively in agreement with a phonon resonant scattering process involving the Zeeman levels of the Co^{2+} . Morigaki's electron spin resonance measurement shows that the internal field splitting of the $J_z = \pm 1/2$ and $J_z = \pm 3/2$ states is 1.34 cm^{-1} , the correct magnitude to cause the conductivity dip in the zero field curve. A Debye conductivity integral with a resonant relaxation rate is employed to calculate the thermal conductivity. The deduced line width from the zero field conductivity curve cannot be explained using a one phonon direct transition process. However, due to the high concentration of Co^{2+} and the lack of inversion symmetry for substitutional sites of Cd^{2+} , one may attribute the line broadening mechanism mainly to the dipole-dipole interaction and the random electric fields.

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I. INTRODUCTION

The theory of lattice thermal conductivity is well documented in several review articles.^{1,2} The finite heat conduction in solids is caused by various phonon scattering processes. These scattering processes are characterized by appropriate relaxation rates which may be temperature and frequency dependent. The objective of measuring thermal conductivity for any controllable imperfections is to find the relaxation rate for that specific imperfection in solids. Extensive experimental and theoretical work has been done to obtain the relaxation rate for each of the phonon scattering processes. One of the important mechanisms is resonant scattering of phonons. This phenomenon was earlier observed by Pohl as a 'dip' in the thermal conductivity curve of KCl containing KNO_2 .³ The result was interpreted as a resonant scattering by NO_2 molecules. A relaxation rate in a Lorentzian form was used to fit his data. Since then many forms of resonant relaxation rate have been applied to numerous conductivity data. These resonant relaxation rate expressions invariably contain different frequency dependences and arbitrary parameters to suit the particular experiment.

Recently, Klein⁴ used the Green function formalism to derive a general phonon resonant relaxation rate which is applicable to the cases where the impurity ion with internal degrees of freedom has two energy levels, such as a two level tunneling or spin system. Klein's expression contains no arbitrary constants provided one knows the line width of the transition. Also his expression is readily adapted to include inhomogeneous line broadening. This theory was first applied to alkali halide crystals containing hydroxide ions⁵ where tunneling

energy levels exist. Because there are seven possible transitions within the main phonon frequency region, these complicate the application of Klein's theory. A candidate to test this theory is a CdS crystal containing cobalt ions. The Co^{2+} substitutes for the Cd^{2+} and is in the tetrahedral sulphur coordination. The ground state of Co^{2+} in this tetrahedral field is an orbital singlet, which is split into two Kramers doublets by the combined action of the trigonal field and the spin-orbital interaction. The energy level diagram deduced from ESR measurement by Morigaki⁶ is shown in Fig. 1. In the absence of an external magnetic field, the separation of the two Kramers doubles $J_z = \pm 1/2$ and $J_z = \pm 3/2$ is 1.34 cm^{-1} . One may consider them as a simple two-level system in zero field. If this two-level system could indeed scatter phonons, then the conductivity curve should reveal a 'dip' around 0.5 K as obtained from the relation⁷

$$\omega_r (\text{cm}^{-1}) \approx 2.67 T_{\text{dip}} (\text{K}) \quad (1)$$

where ω_r is the resonant frequency and T_{dip} is the corresponding conductivity-dip temperature. Furthermore, in this temperature region, the only other important competing process is boundary scattering which is independent of temperature and frequency. This makes the analysis somewhat easier. With the external magnetic field, there will be four distinct energy levels. The number of possible transition increases from one to six. The situation is then similar to the case of the alkali halides containing hydroxide.

II. EXPERIMENTAL METHOD AND RESULTS

The thermal conductivity measurements were taken in a conventional ^3He cryostat. A magnetic field of up to 30 kG was generated by a superconducting solenoid. The cryostat and the measuring techniques are described elsewhere.⁸ From this experiment we found that the resistance versus temperature calibration for the 12 ohm and 68 ohm 1/8 watt nominal value Ohmite resistor in an external field up to 20 kG has no significant change so long as the resistors are kept at liquid helium temperature.

The cadmium sulfide crystal used in this investigation was grown by the Eagle Picher Corporation with a modified Bridgeman technique. The dopant CoS was initially added to the melt in a quantity to allow for an average concentration of 500 ppm of Co^{2+} . Moore and Klein⁹ have previously measured this specimen and several others which are either pure or with different dopants in a temperature region above 1.4 K. Their spectroanalysis shows less than 40 ppm of unintended impurities in this lot of specimens.

We have measured the thermal conductivity of the CdS crystal containing about 500 ppm of Co^{2+} from 0.35 to 4.0 K with the heat flow along the hexagonal axis of the specimen. The result with zero external field is shown in Fig. 2. In this figure we also put in Moore and Klein's data for this and a pure specimen for comparison. The conductivity curve of the doped crystal has nearly a T^3 dependence above 0.7 K and then approaches the pure crystal curve. This constitutes a conductivity 'dip' around 0.5 K as expected if the phonon resonant scattering process dominates.

We have also measured the conductivity of our sample in the presence of six external magnetic fields up to 20.3 kG. The results are shown in Fig. 3. The 4.0, 8.2 and 10.7 kG curves have virtually the same values above 1.5 K, as have the 12.3, 16.4 and 20.3 kG curves above 1.5 K. But below 1.2 K, these curves show the conductivity 'dip' shifted to higher temperature with increasing external field.

III. ANALYSIS AND DISCUSSION

From the elastic constant measurement of CdS, Gerlich¹⁰ finds that the ratios C_{11}/C_{33} , C_{12}/C_{13} and $2C_{44}/(C_{11}-C_{12})$ are close to unity. This is an indication that CdS is nearly isotropic. We therefore employ an isotropic Debye model to analyze our conductive data. The Debye thermal conductivity integral is

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

where k_B is the Boltzmann constant, $\hbar$ is the Planck's constant, v is the average phonon velocity, x is defined as $\hbar\omega/k_B T$, θ_D is the Debye Temperature and $\tau_c(x, T)$ is the combined phonon relaxation time.

The Debye temperature θ_D is 219.3 K as extrapolated to 0 K from Gehrlich's elastic constant data with the isotropic Voigt-Reuss-Gilvary average. Then the average phonon velocity v under this approximation is defined as

$$v = \frac{k_B}{\hbar} \left(\frac{\Omega_0}{12\pi^2} \right)^{1/3} \theta_D = 2.21 \times 10^5 \text{ cm/sec}, \quad (3)$$

where $\Omega_0 = 4.97 \times 10^{-23} \text{ cm}^3$ is the volume of a unit cell.

The combined phonon relaxation rate can be expressed as

$$1/\tau_c = \sum_i 1/\tau_i, \quad (4)$$

where $1/\tau_i$ characterizes each possible phonon scattering mechanism.

Here, the important scattering mechanisms are boundary, isotope, point defect, and resonant.

The theoretical boundary-scattering relaxation rate¹¹ is

$$1/\tau \text{ (boundary)} = v/1.12 \pi d = 8.4 \times 10^5/\text{sec}, \quad (5)$$

where $d = 0.39$ cm and the finite length correction factor η is 0.6 as given by Berman et. al.¹² Klemens¹³ has derived the relaxation rate due to isotopes and isolated point defects. This is expressed by

$$1/\tau \text{ (isotope and point defect)} = \frac{\Omega_0}{4\pi v^3} \omega^4 (S_0^2 + S^2), \quad (6)$$

$$S_0^2 \text{ (isotope)} = \sum_i f_i (1 - M_i/M)^2, \quad (6a)$$

$$S^2 \text{ (point defect)} = n \left[\left(\frac{\Delta M}{M} \right)^2 + 2 \left(\frac{\Delta F}{F} - 13.44 \frac{\Delta R}{R} \right)^2 \right], \quad (6b)$$

where f_i is the fractional concentration of the i th isotope, M_i is the mass of the i th isotope, n is the fractional defect concentration, ΔM is the mass difference between host and impurity atom, ΔF is the change in the coupling constant, ΔR is the change in the nearest-neighbor distance, and M is the average molecular mass. There are eight isotopes of cadmium and four of sulphur. Using their masses and relative abundances, we find

$$1/\tau \text{ (isotope)} = 8.4 \times 10^{-44} \omega^4 \text{ sec}^3. \quad (7)$$

As there are 500 ppm of Co^{2+} in the sample, we should be able to calculate S^2 according to Eq. 6b. But since the quantities $\Delta F/F$ and $\Delta R/R$ are not accurately known, S^2 can only be estimated. First considering the mass difference alone, the relaxation rate is

$$1/\tau \text{ (mass defect)} = 4.0 \times 10^{-44} \omega^4 \text{ sec}^3. \quad (8)$$

CoS has a slightly different crystal structure from CdS , which will cause

the difference in coupling constant. Furthermore, since the ionic radius of Cd is quite different from that of Co, we should expect a large contribution to S^2 . The point defect relaxation rate used here is chosen to be

$$1/\tau \text{ (point defect)} = 15.4 \times 10^{-44} \omega^4 \text{ sec}^3 . \quad (9)$$

We calculate the thermal conductivity with a combined relaxation rate including boundary, isotope and point defect,

$$1/\tau_c = 8.4 \times 10^{+5}/\text{sec} + 23.8 \times 10^{-44} \omega^4 \text{ sec}^3 . \quad (10)$$

The result is shown as curve A in Fig. 4. This curve has a T^3 dependence at temperature below 1.2 K which is quite different from the zero magnetic field conductivity data. Increasing the point defect scattering strength further depresses the conductivity above 1 K and does not fit the data.

To include the resonant scattering, we choose Klein's relaxation rate, which is

$$1/\tau \text{ (resonant)} = \frac{nd}{3\pi\rho(\omega)} \frac{\Gamma(\omega,0) \Gamma(\omega,T) S(T)}{(\omega^2 - \omega_r^2)^2 + \Gamma^2(\omega,T)} , \quad (11)$$

where d is the degeneracy of the resonance, and ω_r is the resonance frequency. Also the density of states $\rho(\omega)$ is defined as

$$\rho(\omega) = \frac{\Omega_0}{4\pi^2 v^3} \omega^2 , \quad (12)$$

and is normalized to unity. The temperature dependent strength $S(T)$ for the two level system is

$$S(T) = \tanh \left(\frac{\hbar\omega_r}{2k_B T} \right) . \quad (13)$$

The temperature dependent half width of the resonance at half maximum $\Gamma(\omega, T)$ can be expressed as

$$\Gamma(\omega, T) = \Gamma(\omega) \coth \left(\frac{\hbar\omega_r}{2mk_B T} \right), \quad (14)$$

where m is equal to unity for a direct one phonon mechanism. The frequency dependent half width $\Gamma(\omega)$ for the spin system is

$$\Gamma(\omega) = \Gamma(\omega_r) \left(\frac{\omega}{\omega_r} \right)^3. \quad (15)$$

We define the reduced half-width $\gamma(T)$ at the resonance frequency to be

$$\gamma(T) = \Gamma(\omega_r, T) / \omega_r^2. \quad (16)$$

Using Eqs. 12 - 16, the resonant relaxation rate becomes

$$\frac{1}{\tau_r} \equiv \frac{4\pi n d v^3}{3\Omega_0} \frac{\gamma^2(0) \tanh \left(\frac{\hbar\omega_r}{2k_B T} \right) \coth \left(\frac{\hbar\omega_r}{2mk_B T} \right) \left(\frac{\omega}{\omega_r} \right)^4}{\left[\left(\frac{\omega}{\omega_r} \right)^2 - 1 \right]^2 + \gamma^2(0) \coth^2 \left(\frac{\hbar\omega_r}{2mk_B T} \right) \left(\frac{\omega}{\omega_r} \right)^6}. \quad (17)$$

For our zero field data, $d = 1$ and $\omega_r = 1.34 \text{ cm}^{-1}$. The two unknown quantities are m and $\gamma(0)$. We add this expression to the combined relaxation rate in Eq. 10 and fit the zero field conductivity data by adjusting m and $\gamma(0)$. The value of m strongly influences the temperature dependence of the calculated conductivity curve. Although several values of m have been considered, $m = 3$ gives the only curve which comes close to the observed temperature dependence of the conductivity. The other parameter $\gamma(0)$ mainly affects the magnitude of the calculated conductivity curve. The best fitted result is shown as

curve B in Fig. 4 where m is 3 and $\gamma(0)$ is 3.88×10^{-4} . The half-width of the resonance Δ is

$$\Delta = \frac{\omega_r}{2} \gamma(0) = 2.6 \times 10^{-4} \text{ cm}^{-1}. \quad (18)$$

Orbach¹⁴ has derived a relaxation rate for a one phonon direct process between two spin states which is equivalent to the expression in Eq. 11 except for m being unity. We identify the half-width with Orbach's spin lattice relaxation time t_1 ,

$$\Delta = 1/t_1(0) = \frac{3\omega_r^3}{2\pi\rho_0 h^5} |\langle a|V_{01}|b\rangle|^2 \quad (19)$$

where ρ_0 is the mass density and $|\langle a|V_{01}|b\rangle|$ is the strength of the one phonon transition between $|a\rangle$ and $|b\rangle$. Using our measured half-width in Eq. 18, we deduce $|\langle \pm \frac{1}{2} | V_{01} | \pm \frac{3}{2} \rangle|$ to be 976 cm^{-1} which is unreasonably large for this type of solid. We may rule out the one phonon direct process in our sample and hence the inhomogeneous broadening mechanisms dominate the scattering process. Assuming that the inhomogeneous scattering rate can be expressed in the form of Eq. 17 with γ replaced by the inhomogeneous line width, then the half-width in Eq. 18 corresponds to the measured inhomogeneous line width.

There are two possible inhomogeneous line broadening mechanisms which contribute to the half-width. First, because of the high concentration of Co^{2+} in the sample, we consider the line broadening due to dipole-dipole interaction. When we use Kittel and Abraham's¹⁵ expression the half-width due to 500 ppm of Co^{2+} is found to be $.33 \times 10^{-4} \text{ cm}^{-1}$, which is 13% of the measured half-width. Furthermore, because the

substitutional sites of Cd^{2+} lack inversion symmetry, the line broadening due to the random electric fields must also be considered. With 500 ppm of Co^{2+} in CdS, it is reasonable to assume that there are 20 ppm of doubly charged defects such as vacancies in the sample.¹⁶ Taking the electric field coupling constant to be about 10^{-4} cm^{-1} according to the expression derived by Mims et.al.¹⁷ With these two line broadening mechanisms, we have accounted for our measured half-width.

In the presence of applied magnetic field, there are four distinct states and six possible transitions. The resonant relaxation rate becomes

$$\frac{1}{\tau_r} = \frac{n}{3\pi} \sum_{i=1}^6 \frac{\gamma_i^2(0) \tanh\left(\frac{\hbar\omega_i}{2k_B T}\right) \coth\left(\frac{\hbar\omega_i}{2mk_B T}\right) \left(\frac{\omega}{\omega_i}\right)^4}{\left\{ \left[\left(\frac{\omega}{\omega_i}\right)^2 - 1 \right]^2 + \gamma_i^2(T) \left(\frac{\omega}{\omega_i}\right)^6 \right\} \rho(\omega_i)} \quad (20)$$

where ω_i is the resonant frequency for the i th transition. We adjust $\gamma_i(0)$ for each transition to obtain the best fit to our data. The fitted conductivity curves for magnetic fields of 4.0 kG and 12.3 kG are shown in Fig. 5 and Fig. 6 respectively. The reduced line width $\gamma_i(0)$ ranges from 6×10^{-5} to $4 \times 10^{-3} \text{ cm}^{-1}$. Because the fitting process involves so many parameters, the $\gamma_i(0)$ used here are by no means the optimal values.

IV. CONCLUSION

The thermal conductivity of CdS containing 500 ppm of Co^{2+} has been measured as a function of temperature from 0.35 to 4.0 K in several external magnetic fields up to 20 kG. We determine that the phonon resonant scattering may be interpreted as due to the spin energy levels of the cobalt ions by employing an isotropic Debye model with Klein's resonant relaxation rate expression to analyze the data. We conclude that the observed resonance is not due to the one phonon direct process and that the deduced line width is probably due to dipole-dipole interaction and random electric field effect.

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FIGURE CAPTIONS

- Figure 1. Energy-level scheme for Co^{2+} in CdS. The numbers in parenthesis refer to the external magnetic field applied to the sample.
- Figure 2. Thermal conductivity of CdS in zero field.
- Figure 3. Thermal conductivity of $\text{CdS}:\text{Co}^{2+}$ in six external magnetic fields. The 4.0, 8.2 and 10.7 kG conductivity curves have the same magnitude above 1.2 K. The 12.3, 16.4, 20.3 kG conductivity curves also have the same magnitude above 1.2 K.
- Figure 4. Theoretical curve and experimental thermal conductivity data for $\text{CdS}:\text{Co}^{2+}$ in zero field. Theoretical curve (A) includes the boundary, isotope and point defect scattering. Theoretical curve (B) includes the resonant scattering term in addition to Eq. 10.
- Figure 5. Theoretical curve and experimental thermal conductivity data for $\text{CdS}:\text{Co}^{2+}$ in 4.0 kG.
- Figure 6. Theoretical curve and experimental thermal conductivity data for $\text{CdS}:\text{Co}^{2+}$ in 12.3 kG.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6