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Thermal Conductivity in Perovskites

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A three-phonon interaction mechanism is proposed to account for thermal-conductivity data in $SrTiO_3$ and $KTaO_3$. The model qualitatively explains the observed strong resonant scattering, its temperature and electric field dependence, and the differences between the two materials.

In a recent paper in this journal, Steigmeier[1] has presented data on the electric field dependence of the thermal conductivity of the perovskites $SrTiO_3$ and $KTaO_3$. Similar data in $SrTiO_3$ has been obtained by Sievers and Pohl,[2] and the thermal conductivity in both materials in zero field has been measured by Holland.[3]

These data have a number of unusual features. The high-temperature range in $SrTiO_3$ has been treated theoretically by Nettleton[4] and will not be discussed here. At low temperatures, both materials have abnormally low conductivity. $KTaO_3$ shows a dip at about 8 °K which looks very much like a strong resonant scattering of the heat-carrying thermal phonons. The thermal conductivity κ for $KTaO_3$ is relatively insensitive to electric field. However, for $SrTiO_3$, κ does depend on field. Steigmeier was able to fit his data in $SrTiO_3$ by assuming that, in addition to boundary and isotope scattering, there was a resonant scattering mechanism whose contribution to the total scattering rate had the following purely empirical form:

$$\tau_{\text{res}}^{-1}=C_1\omega^2T^2/\{[\omega^2-\omega_r(T)^2]^2+C_2\omega_r(T)^2\omega^2\}\,, \qquad (1)$$

where ω is the frequency of the thermal phonon being scattered, and T is the absolute temperature. $\omega_r(T)$ is the resonant frequency. At zero electric field, $\omega_r(T)$ was taken to be equal to $\omega(0, \text{TO})$, the frequency of the "soft" TO phonon mode at $\vec{k}=0$, where $\vec{k}$ is the wave vector, but no justification for this choice was given. C_1 and C_2 were treated as adjustable parameters. C_2 came out quite large (~ 3.7), so the resonance was very broad. The effect of an electric field $\vec{E}$ is to raise $\omega(0, \text{TO})$ in a manner determined by the well-known Lyddane-Sachs-Teller[5] (LST) relation. However, Steigmeier found that Eq. (1) did not fit his field-dependence data if he took for $\omega_r(T)$ the value of $\omega(0, \text{TO})$ calculated from the LST relation using the known electric field dependence of the static dielectric constant. Instead, he had to treat ω_r at each field value as an additional adjustable parameter $\omega_r(\vec{E})$. The resonant frequency was found to be considerably less sensitive to field than was $\omega(0, \text{TO})$. For example, at 20 kV/cm and 15 °K, ω_r was only 1.6 times its zero-field value while $\omega(0, \text{TO})$, for phonons polarized parallel to $\vec{E}$,[6] had increased fourfold according to the LST relation.

Although it does account phenomenologically for the data, Steigmeier's analysis is unsatisfying for several reasons. First, although he suggests that an interaction between the longitudinal acoustic (LA) branch and the TO branch dominates the thermal resistance, he does not provide an explanation for the resonant character of the interaction or specify why $\omega(0, \text{TO})$ should be the resonant frequency. The accidental degeneracy of the TO and LA modes does not occur at $\vec{k}=0$, and, in any event, degeneracy between two phonon modes does not result in a resonant scattering. Second, there is no explanation for the broadness of the resonance. Third, an interaction involving a TO phonon at $\vec{k}=0$ is necessarily a normal, $\vec{k}$-conserving process and normal processes by themselves do not lead to thermal resistance. Fourth, no justification for the particular form of Eq. (1) was given. Finally, there is the incorrect behavior with electric field described above. In this note we suggest a physical mechanism which can remove most of these objections and account for Steigmeier's data, at least qualitatively.

An essential assumption for this proposal is that the heat is carried entirely by the transverse acoustic (TA) branch phonons. This assumption is plausible because LA phonons are scattered strongly by the soft mode, both through Akhieser-type interactions[7] and by four-phonon processes.[4] Also, the LA branch has a smaller specific heat than the TA branch and has a slightly larger thermal resistivity due to phonon scattering by tetragonal domains.[8] However, a good quantitative calculation of the net LA thermal conductivity does not appear to be possible at this time, and we must emphasize that its neglect is strictly an assumption.

The proposed resonant scattering mechanism for the TA phonon is illustrated in Fig. 1. A TA phonon of wave vector $\vec{k}_1$ can combine with a TO phonon of wave vector $\vec{k}_2$ to produce another TO phonon having wave vector $\vec{k}_1+\vec{k}_2$. It is easy to see that this process has a broad resonant character. As illustrated in Fig. 1, the resonant frequency may be determined by graphical construction, setting $\vec{k}_2=0$. Because the exact shape of both the TO and TA dispersion relations as obtained from neutron data is uncertain, ω_r cannot be determined very accurately by this construction, but it is surely comparable to $\omega(0,\ \text{TO})$.[9] The broadness of the resonance is also accounted for by this mechanism: TA phonons with $\omega \neq \omega_r$ simply choose TO phonons of the proper $\vec{k}_2$ to interact with (see Fig. 1). These nonresonant interactions are weaker because the much smaller TO population will more than offset the increased TO density of states $\vec{k}_2$.

It can be shown that the proposed mechanism has roughly the right strength. This process has been considered by Dvorak[10] in a calculation of the soft-mode linewidth. His results are readily modified to obtain the TA mode relaxation time; order of magnitude agreement with Eq. (1) is found. The temperature dependence of the proposed mechanism is also reasonable. At resonance, the scattering rate is roughly proportional to the population of the $k=0$ soft mode (since only low temperatures are important and the population of the TO mode at $\vec{k}_1+\vec{k}_2$ is therefore negligible). In other words, we expect

$$\tau_{\text{res}}^{-1}(\omega=\omega_r)\propto\{\exp[\hbar\omega(0,\text{TO})/k_BT]-1\}^{-1}\quad,\qquad(2)$$

with k_B being Boltzmann's constant. Direct calculation, using data from Steigmeier's Table II, shows this dependence to be very close to the T^2 behavior (on resonance) given by Eq. (1) over the range 5–20 °K. Therefore, Eq. (2) should be equally as good as Eq. (1) in describing the data.

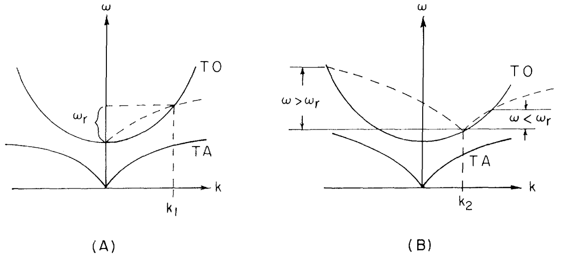

FIG. 1. Schematic representation of the proposed resonant scattering mechanism: $\text{TA}(\vec{k})+\text{TO}(\vec{k}_2)\rightarrow\text{TO}(\vec{k}_1+\vec{k}_2)$. The left-hand diagram is for the resonant condition $\vec{k}_2=0$. The right-hand diagram is for the nonresonant case $\vec{k}_2\neq 0$. In both cases, the dashed lines represent the TA branch redrawn with the origin at $\vec{k}_2$ in order to determine the allowed interactions. The nonresonant interactions are weaker because the thermal population of the TO mode at $\vec{k}_2$ is smaller than that at $k=0$. An examination of the actual dispersion curves for $SrTiO_3$ and $KTaO_3$ shows that the analogous process for LA phonons is not energetically possible.

Finally, this mechanism accounts qualitatively for the electric field dependence of ω_r. From Fig. 1, the variation of ω_r with E is seen to arise not from the change in $\omega(0,\text{TO})$, but from the E dependence of the *shape* of the TO dispersion. If the effect of the electric field were simply to shift the TO branch upward uniformly, the resonant strength would change, but the resonant frequency would not. Thus, it is not surprising that ω_r is less sensitive to E than is $\omega(0,\ \text{TO})$.

The mechanism proposed above is an N process, and we must, therefore, explain how it influences κ. The scattering transfers excitation from a TA mode to a TO mode with approximately the same $\vec{k}$ and group velocity. However, the square of the Gruneisen constant for the TO mode $\gamma^2(\text{TO})$ will be perhaps 10^4 times γ^2 for the original TA mode.[7] Thus, the created TO phonon is much more easily scattered by the strain fields of dislocations or impurities. Since these are U processes, a thermal resistance ensues, but the net relaxation rate may be limited by the TA + TO → TO N process.

On this model, the difference between the thermal conductivity of $SrTiO_3$ and $KTaO_3$ comes about since $\omega(0,\text{TO})$ for $KTaO_3$ at low temperature is about a factor of 2 larger than for $SrTiO_3$. This makes the TO mode much less sensitive to an electric field. It also leads to a smaller resonant scattering at low temperature since the soft mode depopulates much more rapidly. Thus at 2 °K, the thermal conductivity in $KTaO_3$ is understandably a factor of 30 larger than in $SrTiO_3$.

In conclusion, the proposed TA + TO → TO scattering mechanism *qualitatively* accounts for Steigmeier's data in the following respects: (1) It has approximately the same mathematical form as was used heuristically by Steigmeier, giving about the right interaction strength, resonant frequency, resonance width, and temperature dependence. (2) It explains why the electric field dependence of the resonant frequency is weaker than that of the $\vec{k}=0$ soft-mode frequency. (3) It explains how the heat flow is ultimately dissipated by U processes even though the rate is limited by N processes. (4) If explains the differences between $KTaO_3$ and $SrTiO_3$. A more quantitative treatment of this interaction would require more detailed neutron data, a measurement of the g_{44} electrostrictive constant in order to determine the TO-TA coupling strength,[10] and some knowledge of the E dependence of $\omega(\vec{k},\ \text{TO})$ for $\text{k}\neq 0$.

[1] E. F. Steigmeier, Phys. Rev. 168, 523 (1968).

[2] A. J. Sievers and R. O. Pohl, Proceedings of the Fourth Conference on Thermal Conductivity, San Francisco, 1964 (unpublished).

[3] H. H. Barrett and M. G. Holland, IEEE Ultrasonics Symposium, Vancouver, B.C., 1967 (unpublished).

[4] R. E. Nettleton, Phys. Rev. 140, A1453 (1965).

[5] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. 59, 673 (1941).

[6] P. A. Fleury and J. M. Worlock, Phys. Rev. 174, 613 (1968).

[7] H. H. Barrett, Phys. Rev. 178, 743 (1969); *Physical Acoustics*, edited by W. Mason and R. N. Thurston (Academic, New York, 1970), Vol. 6, Chap. 2.

[8] F. W. Lytle, J. Appl. Phys. 35, 2212 (1964).

[9] The most precise neutron data for $SrTiO_3$ is that of Y. Yamada and G. Shirane [J. Phys. Soc. of Japan 26, 396 (1969)]. From this data, graphical construction shows that ω_γ is about 10% lower than $\omega(0, \mathrm{TO})$ for both the [110] and [100] directions at 4.2 °K and about 25% lower for the [100] direction at 78 °K.

[10] V. Dvorak, Czech. J. Phys. B17, 726 (1967). (Note that this paper contains a serious numerical error. His parameter α should be about 2×10^{-2} cm^2 Hz instead of $\approx 10^{-1}$ cm^2 Hz. The numerical lifetime values are, therefore, incorrect.)

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ERRATA

Frequency Spectra of Body-Centered-Cubic Lattices, B. C. Clark, D. C. Gazis, and R. F. Wallis [Phys. Rev. 134, A1486 (1964)]. Equation (10) should read $ac_{12}=2(\alpha-3\gamma_1-\frac{3}{2}\gamma_2)$ rather than $ac_{12}=2(\alpha-3\gamma_1+\frac{3}{2}\gamma_2)$.

Polariton Theory of Resonance Raman Scattering in Insulating Crystals, B. Bendow and J. L. Birman [Phys. Rev. B 1, 1678 (1970)]. Equation (2.9) was typeset incorrectly. It should read

$$\frac{d\sigma}{d\Omega}=(2\pi)^{-2}\sum_{\gamma\gamma'}|\alpha(k_\gamma,\gamma)|^2|\alpha[k'(\gamma\gamma'),\gamma']|^2[k'(\gamma\gamma')]^2$$
$$\times\{v_g(k_\gamma,\gamma)v_g[k'(\gamma\gamma'),\gamma']\}^{-1}|\langle k_\gamma,\gamma|T|k'(\gamma\gamma'),\gamma'\rangle|^2.$$

Also, Eq. (4.4) should contain the expression $|V(\vec{\mathrm{k}},\vec{\mathrm{k}}')|^2$ instead of $V(\vec{\mathrm{k}},\vec{\mathrm{k}}')$.

Band Shape and Phonon Broadening of *U* Bands in Alkali Halides, S. S. Mitra, R. S. Singh, and Y. Brada [Phys. Rev. 182, 953 (1969)]. Equations (1), (2), and (5) were misprinted. The corrected equations are

$$M_n=\int_{\mathrm{band}}\alpha(\epsilon)\epsilon^n\,d\epsilon\ , \tag{1}$$

$$m^2=(1/M_0)\int_{\mathrm{band}}\alpha(\epsilon)(\epsilon-\bar{\epsilon})^2d\epsilon\ , \tag{2}$$

and

$$G(P)=S^Pe^{-S}/P!\ . \tag{5}$$

Results quoted in the paper are for the correct equations.

Photoreflectance Line Shape at the Fundamental Edge in GaAs, J. L. Shay [Phys. Rev. B 2, 803 (1970)]. The printer dropped Fig. 4, which was present in the galleys.

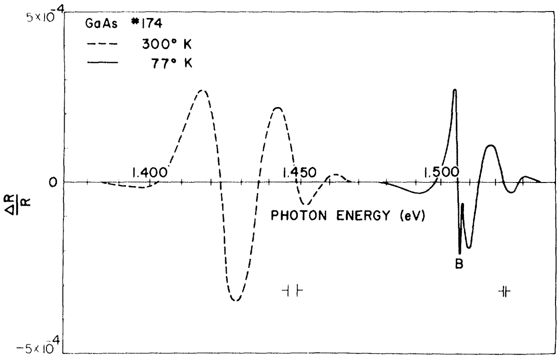

FIG. 4. Temperature dependence of the photoreflectance line shape.