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ROLE OF FINITE LATTICE HEAT CAPACITY AND KAPITZA THERMAL RESISTANCE IN PARAMAGNETIC RELAXATION UNDER PHONON SUPERHEATING CONDITIONS

V. A. ATSARKIN

Institute of Radio Engineering and Electronics, Academy of Sciences, U.S.S.R.

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An analysis is made of the conditions under which an increase of temperature of the entire crystal lattice can occur during paramagnetic spin-lattice relaxation. The case of a "phonon bottleneck" is considered, in which the energy of the superheated "resonant phonons" is conveyed to the lattice oscillations of different frequencies. Solution of the heat balance equations permits one to find the criteria for estimating the degree of crystal heating and the characteristic times for the establishment of equilibrium. It is shown that when the crystal is cooled in liquid He II, the Kapitza boundary thermal resistance plays an important role. Application of the proposed model to an explanation of the experimental results of Griffiths and Glättli on paramagnetic relaxation in praseodymium ethyl sulfate leads to good agreement of the theory with experiment, which confirms the possibility of strong scattering of the resonant phonons with a change in their frequencies. Possible causes of such a phenomenon are discussed.

PARAMAGNETIC spin-lattice relaxation at low temperatures can under certain conditions give rise to a so-called "phonon bottleneck" (superheating of phonons that "resonate" with the spins). This phenomenon is observed when the direct spin-lattice interactions predominate, and the heat capacity c_P of the phonons at the paramagnetic-resonance frequency ν_0 (within the line width $\Delta\nu$) is much less than the heat capacity c_S of the spin system, with this the temperature of the phonons resonant with the spins can rise substantially higher than the equilibrium temperature. The phonon bottleneck effect has been studied in detail theoretically,[1-7] and recently experimentally as well.[8-14] In the presence of a phonon bottleneck, the experimentally observed time, τ, of recovery of the paramagnetic resonance-absorption signal after switching off the saturating power is significantly greater than the true spin-lattice relaxation time τ_S. The time τ is approximately equal to $\tau_P c_S/c_P$,[8] where τ_P is the lifetime of a phonon of frequency ν_0 and determines the rate at which equilibrium sets in between the resonant phonons and the thermostat. The heat capacity of the thermostat is usually taken as infinite. However, this assumption is really true only when the energy of the superheated phonons is conveyed directly to the helium bath. If their energy passes by some means into the remaining lattice modes, then, under certain conditions which are considered below, it is necessary to take into account the finite heat capacity of the crystal as a whole.

Until now, the possibility of increasing the temperature of the entire crystal in paramagnetic relaxation has been discussed only outside the context of the problem of superheated resonant phonons,[15-16] so that the results of these works could not be applied directly to the majority of experiments. We note that Peterson,[16] considered the rather unrealistic case of a completely thermally isolated crystal is and made an error in the numerical estimates, because of which the size of the expected effects is exaggerated by three orders of magnitude.

The establishment of thermal equilibrium between the superheated resonant phonons and the entire phonon spectrum can occur only if the time τ_P is determined by the probability of phonons scattering with a change in frequency and is shorter than the time necessary for the escape of a phonon from the crystal into the helium bath. In fact, in many cases (ethyl sulfates doped with neodymium [8] or praseodymium,[14] and copper Tutton salts [13]) the phonon lifetime determined from experimental values of the relaxation time τ under conditions of a phonon bottleneck actually appears to be much shorter than the value of l/v, where l is the size of the crystal, and v is the speed of sound.

We also note the experimental observation[11,14,17] of an abrupt reduction of the time τ when the liquid helium which cools the crystal becomes superfluid (H II). This phenomenon is undoubtedly related to the change in thermal resistance of the medium surrounding the crystal, and suggests convincingly the possibility of an increased temperature of the crystalline lattice during relaxation in the presence of a phonon bottleneck.

Thus the transfer of energy from the superheated resonant phonons to the remaining lattice vibrations is quite possible, at least in a large number of paramagnetic crystals. To understand the consequence of such transfer, it is necessary to take into account the finiteness of the lattice heat capacity and the thermal resistance of the medium, which is determined in the most important case (He II) by the Kapitza boundary resistance.[18]

We consider a system consisting of four reservoirs: spin system S, phonon system P containing the resonant phonons having frequencies in a band $\Delta\nu$ approximately equal to the EPR line width, lattice system L containing all the vibrational modes of the crystal, and bath B having infinite heat capacity. We assume that contact between the subsystems takes place only by the scheme $S \longleftrightarrow P \longleftrightarrow L \longleftrightarrow B$. In particular, we neglect the direct transfer of energy from the resonant phonons to the bath. To each reservoir we ascribe a corresponding specific heat c_i and temperature T_i. We assume the heat flow $\dot{u}$ across the boundary of two reservoirs in thermal contact to be proportional to the difference in their temperatures. Then we can write

$$\begin{aligned} \dot{u}_S &= c_S\dot{T}_S = \frac{c_S}{\tau_S}(\dot{T}_P - \dot{T}_S), \\ \dot{u}_P &= c_P\dot{T}_P = \frac{c_S}{\tau_S}(\dot{T}_S - \dot{T}_P) + \frac{c_P}{\tau_P}(\dot{T}_p - \dot{T}_P), \\ \dot{u}_L &= c_L\dot{T}_L = \frac{c_P}{\tau_P}(\dot{T}_P - \dot{T}_L) + \frac{c_L}{\tau_L}(\dot{T}_B - \dot{T}_L). \end{aligned} \tag{1}$$

Here τ_L is the characteristic time for the establishment of thermal equilibrium between L and B, equal to rc_LV, where r is the thermal resistance between the lattice and the bath, and V is volume of the sample.

Equation (1), in which temperatures are used in place of particle numbers, is correct only for small deviations from equilibrium (i.e., for a small degree of saturation; all differences must satisfy $|T_i - T_j| \ll T_B$). Since the asymptotic behavior of the saturation decay curve is usually studied in investigations of the phonon bottleneck, such a consideration is quite justified.[7]

To determine the conditions for which a significant increase in T_L can be expected, one must solve Eqs. (1) assuming continuous saturation of the EPR signal by an rf field. By this means, it is not difficult to show that, in the presence of phonon bottleneck we have

$$\Delta T_L \approx \Delta T_S / (1 + c_L\tau_P c_P^{-1}\tau_L^{-1})$$

so that the criterion for an increase in T_L is

$$c_P/\tau_P \gtrsim c_L/\tau_L = 1/rV. \tag{2}$$

Condition (2) has a simple physical interpretation: the thermal contact between subsystems P and L must not be worse than that between L and B. If the inequality in (2) is great, then $T_L \approx T_S$ and the cooling time for the entire system after removal of the saturation is given by

$$\tau' = r(c_S + c_L)V. \tag{3}$$

The criterion (2) is not always convenient, since it contains τ_P, whose value is usually difficult to estimate. One can show, however, that (2) clearly is fulfilled if

$$\tau \sim rc_SV, \tag{4}$$

where τ is the experimentally observed relaxation time. Notice that Eq. (4) is a sufficient, but not necessary, criterion for an increase in T_L under phonon bottleneck conditions.

The quantity r in Eqs. (3) and (4) includes the thermal resistance r_{cr} of the crystal itself, the boundary thermal resistance, r_b, and the thermal resistance of the surrounding medium (helium) r_m. Boundary resistance (first observed by P. L. Kapitza[18]) arises on cooling the sample with He II and is accompanied by an abrupt change in temperature at the boundary dividing the two media. The thermal conductivity of superfluid helium is practically infinite, and so r_m can be neglected. Comparison of experimentally measured values of r_b[19] with the usual values of thermal conductivity of single crystals at low temperatures (see, e.g.,[20,21]) shows that $r_b \gg r_{cr}$ for a sample thickness of 1 mm. Further, the quantity $r_b = R/S$, where R is the Kapitza resistivity per unit surface S, plays the determining role in the most frequently encountered case of a crystal cooled in liquid He II.

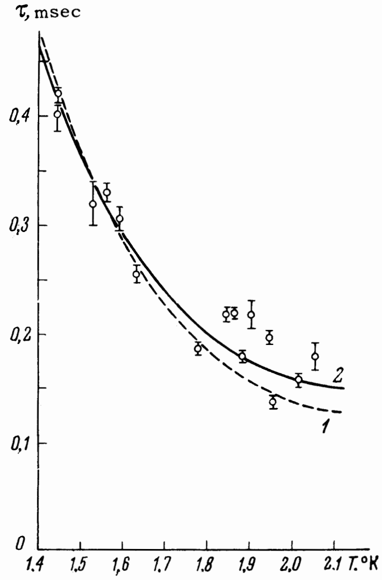
At temperatures above the helium λ-point (2.18°K) one has $r_m \gg r_b$ (for the thermal conductivity of He I, see, e.g.,[22]), and the time τ_L is determined from the solution of the corresponding equation for the thermal conductivity. In any case, τ_L must increase greatly in the transition from He II to He I.

COMPARISON WITH EXPERIMENT

Griffiths and Glättli[17] observed a jump in the paramagnetic relaxation time when a sample of praseodymium ethyl sulfate, of size 3 × 3.5 × 5 mm and cooled in liquid helium was passed through the helium λ-point. These authors, correctly pointing out the decisive role of the helium thermal resistance in the relaxation above the λ-point, assume however that below the λ-point the usual phonon bottleneck occurs without heating of the entire crystal. The strong temperature dependence (T^{-3} to T^{-4}) of τ from 1.4 to 2.1°K is explained by them to be the result of phonon diffusion due to reabsorption by paramagnetic ions.[3,6]

We will show that in this experiment it is not permissible to neglect the effect of the heating of the whole crystal lattice. First, we estimate the upper limit of the phonon mean free path, Λ, due to scattering with a change in frequency. Using the data on experimental conditions and EPR line width cited in the paper of Griffiths and Glättli, and assuming $v = 2 \times 10^5$ cm/sec we obtain, using a Debye distribution, $c_P = 5.85 \times 10^{-7}$ Joule/deg-cm^3 and $c_S = 0.79 \times 10^{-3}$ Joule/deg-cm^3 at T = 1.5°K. The measured relaxation time τ at this temperature is 0.36×10^{-3} sec. Assuming that τ cannot be shorter than $\tau_P c_S/c_P$, we obtain $\tau_P \leq 2.7 \times 10^{-7}$ sec. Thus $\Lambda \leq 5.4 \times 10^{-2}$ cm, i.e., considerably less than the linear dimensions of the sample, so that in this case scattering of the resonant phonons occurs with transfer of their energy to the entire lattice.

To estimate the possibility of a rise in temperature of the crystal we use the sufficient condition (4). We take the value of R from the experimental data of Johnson and Little.[19] These authors showed that for a wide class of solids, including metals, semiconductors, and dielectrics, the Kapitza boundary thermal resistance varies little from substance to substance, and depends weakly on surface condition. For all materials studied by them, it is found that $R = R_0 T^{-n}$, where R_0 varies from 7 to 39 deg-cm^2/volt and n varies from 2.5 to 4.15. In particular, at 1.5°K, the value of R for different materials varies within the small range from 2.4 to 9.5 deg-cm^2/volt. Using these values together with the above values of c_S and τ at 1.5°K, and assuming also that $V/S = 6.1 \times 10^{-2}$ cm. we obtain $\tau = (0.8–3.1) R c_S V/S$. Thus the values of τ and $r c_S V$ are of the same order of magnitude, and one cannot neglect the rise in lattice temperature in this case. It is easy to show using the formulas of Giordmaine and Nash[6] that this conclusion is not changed even when τ is determined by phonon diffusion.



Temperature dependence of the relaxation time in praseodymium ethyl sulfate. Experimental points are data of Griffiths and Glättli; [17] curves 1 and 2 are calculated from Eq. (3) for different values of R.

We turn now to the direct comparison of experimental results[17] with Eq. (3), which corresponds to significant heating of the crystal lattice (we assume that r is determined by the Kapitza boundary resistance). This comparison is facilitated by the fact that the heat capacity of praseodymium ethyl sulfate has been measured experimentally at low temperatures[25] and there is no need to resort to the Debye approximation. The figure shows the time τ' calculated according to Eq. (3) together with the experimental points of Griffiths and Glättli[17] at 2.1°K. Curve 1, which corresponds to a typical value of the Kapitza resistance $R = 22.3\ T^{-3}$ deg-cm^2/volt, agrees satisfactorily with the experimental data; curve 2, calculated with $R = 18\ T^{-2.5}$, agrees even better with the experimental values of τ. The deviation of the temperature dependence of R from the theoretical relation[23,24] $R \sim T^{-3}$ is not surprising in view of the experiments of Johnson and Little[19] mentioned above. The values of R used in the calculation of both curves agree excellently with the experiments of these authors.

Taking into consideration the approximations used, the agreement of theory with experiment, both in the temperature dependence and in the absolute value of τ (see the figure), is very good. Evidently, the condition $c_P/\tau_P \gg c_L/\tau_L$ is in fact satisfied in this example. Thus, one can infer that $\tau_P \ll 2.7 \times 10^{-7}$ sec and $\Lambda \ll 5.4 \times 10^{-2}$ cm, which agrees with the estimates of Larson and

Jeffries[14] for magnetically diluted ethyl sulfates of lanthanum and yttrium doped with praseodymium.

CONCLUSIONS

The considered model of paramagnetic relaxation (spins → resonant phonons → all lattice vibrations → thermostat) in fact can be realized experimentally, and leads to a significant crystal heating. This means that, at least in certain cases, the scattering of phonons with change of frequency plays a decisive role in cooling the phonons "resonating" with the spins. However, estimates of the probability of such scattering due to anharmonicity of the lattice vibrations [1,26] leads to a large mean free path Λ. In fact, using the calculations of Klements,[26] we obtain

$$\Lambda = 1.5\cdot 10^{-20}\frac{\rho v^6}{\Gamma^2}\frac{1}{\nu T^4}, \tag{5}$$

where ρ is the crystal density, and Γ is the Grüneisen constant, which is usually close to 2. For $\rho = 1.8$, $v = 2\times 10^5$ cm/sec, $\nu = 30$ GHz, and $T = 1.5$°K, we find $\Lambda = 2.8$ cm. which exceeds by about a factor of 50 the upper limit for Λ obtained in the preceding section. Scattering from impurities also cannot give a substantial reduction in Λ.[26,5] Thus there clearly exists some additional mechanism for phonon scattering. It has not been excluded here that an important role can be played by the low-lying optical modes of the lattice oscillations. Such a mode, with excitation energy of only 3.4°K, is observed in particular in the ethyl sulfates,[27] where it gives a significant contribution to the thermal conductivity at low temperatures. Equation (5) is obtained without taking the optical modes into account.

Another cause of the lower probability of escape of the resonant phonons to the helium bath can be the reabsorption of the phonons by the paramagnetic ions.[3,6] This phenomenon leads to an increase in the time necessary for the phonons to reach the crystal boundaries, and consequently to an increase in the probability of scattering with transfer of energy to vibrations of different frequencies. Reabsorption of phonons is particularly important in crystals with strong inhomogeneous broadening of the EPR line;[6] just such a situation is observed in praseodymium ethyl sulfate.

We remark that we have observed experimentally an increase in lattice temperature during paramagnetic relaxation, and the associated abrupt change in the time τ in the transition of the hel helium across the λ-point, in crystals of gadolinium hexa-antipyrinate-tri-iodide. A strong inhomogeneous broadening of the EPR line occurs in this substance also.

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