of this extrapolation may be as much as 7%.[10] No reliable calorimetric determination of γ is available of Hg because of the very large low-temperature lattice specific heat of this element.

The temperature dependence of the superconducting electronic specific heat, C_{es}, may be deduced from the relation[2]

$$C_{es}(T)=\gamma T+(VT/4\pi)d^2(H_c^2)/dT^2.$$

However, the aforementioned uncertainty in γ leads to a rapidly increasing uncertainty in $C_{es}(T)$ below $t=0.5$. The only definite conclusion is that, in the temperature range immediately below T_c, C_{es} for Hg drops much more rapidly than the nearly exponential behavior predicted by the theory of Bardeen, Cooper, and Schrieffer.[11]

[10] It should be pointed out that $\lim(dH_c/dT)$ as $T\to 0°$K is much more sensitive to the extrapolation error than is H_0. Thus the present ambiguity regarding γ does not have a serious effect on the form of $D(T)$ shown in Fig. 1. This problem with γ did not arise in the earlier measurements on Pb (reference 2) because of the lower value of t attained in that work.

[11] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

The critical field measurements on Pb and Hg establish that these elements are (a) qualitatively similar, and (b) conspicuously anomalous among the superconducting elements in the character of their electronic excitation spectrum. A more detailed thermodynamic analysis suggests that the positive values of $D(T)$ arise from values of the superconducting energy gap which are substantially larger than the BCS value of 3.52 kT_c. Thus the present results seem to compliment recent observations on Pb and Hg by infrared techniques which show that the sudden onset of absorption in these superconductors occurs at anomalously high frequencies.[12]

Precise measurements of $D(T)$ are being made on other superconducting elements and will be extended to the temperature range below 1°K. Further results will be reported shortly.

We are pleased to acknowledge the assistance of D. C. Hopkins with these measurements, and also D. M. Ginsberg for valuable discussions.

[12] P. L. Richards and M. Tinkham, Phys. Rev. Letters **1**, 318 (1958); D. M. Ginsberg and M. Tinkham, Phys. Rev. (to be published).

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Harmonic Spin Coupling in Ruby

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A new mode of maser pumping which makes use of harmonic spin coupling in ruby has been demonstrated. In addition higher order harmonic spin coupling effects in ruby have been found experimentally.

IN ruby a new mode of maser pumping has been demonstrated. This new mode of pumping makes use of harmonic spin coupling in ruby and indicates the possibility of operating a maser with pumping at frequencies lower than the signal frequency. Coupling between spins possessing the same transition frequency has been demonstrated by Feher and Scovil[1]. They found a reduced relaxation time associated with a gadolinium transition if the transition frequency coincides with that of the cerium transition, both ions being simultaneously present in a diamagnetic ethyl sulfate host crystal. Harmonic spin coupling in ruby was found by Mims and McGee.[2] They found an accelerated relaxation rate associated with a resonance transition in ruby whenever orientation and magnitude of the applied magnetic field were such that there was a 1:1, 2:1 or 1:2 ratio between two transition frequencies in the energy level scheme. In addition Mims and McGee[3] suggested that the harmonic spin coupling effect they observed in their relaxation experiments was only the first in a sequence of higher order processes and they further suggested that harmonic spin coupling might be used to advantage for pumping masers at frequencies beyond the range of existing signal sources.

This note contains experimental results which verify the existence of the higher order harmonic spin coupling processes as suggested by Mims and McGee.[3] Also we have demonstrated that harmonic spin coupling processes can be used in maser pumping. Consider four energy levels in ruby with transition frequencies as indicated in Fig. 1(a). For simultaneous observation of essentially all ruby transitions, a ruby sample in the shape of a rod was placed inside a shorted X-band waveguide with a helical transmission line wound on the sample. Signal transmission through the helix permits the study of lower microwave transition frequencies whereas transition frequencies in the

[1] G. Feher and H. E. D. Scovil, Phys. Rev. **105**, 760 (1957).

[2] W. Mims and J. D. McGee, (unpublished).

[3] W. Mims and J. D. McGee, Bell Telephone Laboratories (private communication).

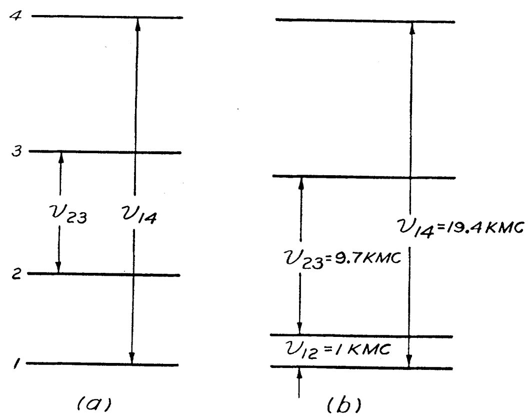

FIG. 1. (a) Typical energy level diagram for ruby. (b) Energy level diagram in ruby for $\theta=90°$ and a magnetic field of 1700 gauss.

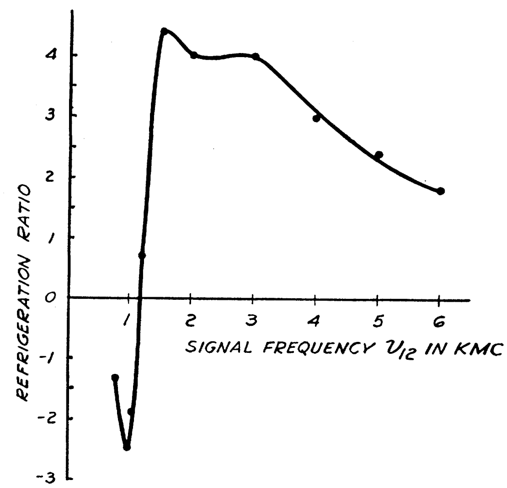

FIG. 2. Plot of the refrigeration ratio versus signal frequency ν_{12} at $\theta=90°$.

X-band range and higher can conveniently be observed by studying the signals reflected from the shorted waveguide. Both methods together allow for a practically continuous coverage of the microwave frequency range. Using this technique, it was observed that if saturating power was applied at ν_{23} then partial or complete saturation of the ν_{14} transition was achieved whenever the condition $\nu_{14}=n\nu_{23}$, with n an integer, was satisfied. In particular for the $\theta=40°$ orientation in ruby effects were seen for $n=3$, 4, and 5 and for the $\theta=90°$ orientation an effect was seen for $n=2$.

For the case of $\theta=90°$ in ruby at a field of 1700 gauss the energy levels are shown in Fig. 1(b). In this operation the complete saturation of the ν_{23} transition at 9.7 kMc/sec produced complete saturation of the ν_{14} transition at 19.4 kMc/sec and spin inversion (emission) at $\nu_{12}=1$ kMc/sec. Normally, if this condition $\nu_{14}=2\nu_{23}$ were not satisfied, pumping at ν_{23} would have produced spin refrigeration (enhanced absorption) rather than spin inversion. The signal frequency region over which maser action by harmonic spin coupling was achieved for $\theta=90°$ in ruby for this mode of operation is shown in Fig. 2. The refrigeration ratio plotted is defined as the ratio of the absorption at ν_{12}, when ν_{23} is saturated, to the absorption at ν_{12}, when the spin system is in thermal equilibrium. Negative refrigeration ratios indicate negative absorption or emission at ν_{12}.

At present the mechanism responsible for harmonic spin coupling in ruby has not been established; however, two possible mechanisms are the direct spin-spin interaction or a spin-phonon-spin process. If the magnetic dipole-dipole interaction is responsible then harmonic spin coupling takes place entirely within the spin system. If, on the other hand, a spin-phonon-spin process is involved then it is imagined that the anharmonic terms in the lattice potential carry out the harmonic or multiplication effects which are coupled to the spins by a phonon-spin interaction. The temperature and concentration dependence[3] of the accelerated relaxation rate observed by Mims and McGee seems to favor the direct spin-spin interaction model at present.

The demonstration of the effects described indicates that one may pump a maser at a frequency lower than the signal frequency by taking advantage of harmonic spin coupling. One would apply pump power at some transition frequency ν_1. By virtue of harmonic coupling, this would lead to saturation at a higher frequency transition $\nu_2=n\nu_1$. Saturation at ν_2 would lead to maser action at a third frequency $\nu_3<\nu_2$ subject to the usual conditions with regard to frequency and relaxation time ratio. This implies the possibility $\nu_3>\nu_1$. It is required in addition, however, that ν_3 is not related in a simple rational ratio to ν_2 or ν_1. This type of maser operation would be of value especially for maser amplification in the millimeter wavelength region where ordinarily submillimeter pump sources would be needed.

The author is indebted to Higa[4] for information about his experimental results prior to publication. Higa studied ruby at the 90° orientation at 1700 gauss with equipment permitting the observation of ν_{12} and ν_{23} only. Disregarding ν_{14}, he expected to find spin refrigeration at ν_{12} upon saturation of ν_{23}. The maser action found instead indicated the presence of an effect which can be identified as harmonic spin coupling.

[4] W. Higa, J. Appl. Phys. (to be published).