PHYSICAL REVIEW VOLUME 116, NUMBER 6 DECEMBER 15, 1959

Relaxation Effects in a Maser Material, $K_3(CoCr)(CN)_6$†

S. Shapiro* and N. Bloembergen
Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts

(Received July 6, 1959)

The rate equations for the occupation of spin levels are augmented to include cross-relaxation processes. It is confirmed experimentally that the latter are important when the concentration of magnetic ions is high or two resonances have a small separation. Maser action is usually impaired under such circumstances. When experimental conditions are chosen such that cross-relaxation effects are negligible, it is shown that all spin-lattice relaxation processes for Cr^{+++} in the cyanide are proportional to the absolute temperature in the liquid helium range. The susceptibilities at both the pump and maser frequencies follow the general theoretical dependence and reach asymptotic values as a function of pump power.

I. INTRODUCTION

Investigation of paramagnetic relaxation[1] by means of microwave resonance techniques[2] has received new impetus[3–5] with the advent of solid-state masers.[6,7] It has recently been shown[8] that cross-relaxation terms have to be added to the conventional rate equations. The present paper is a sequel to BSPA. Some general expressions for the dependence on pump power of the susceptibility at various frequencies are derived and the temperature dependence in the presence and absence of cross-saturation is discussed in Sec. II. A brief description of the experimental method is given in Sec. III. Experimental data are discussed in Sec. IV. Evidence is presented that the various spin-lattice relaxation times in $K_3(CoCr)(CN)_6$ are all inversely proportional to the absolute temperature in the liquid helium range. The theoretical dependence of the susceptibility on pump power is verified. Experiments at different Cr^{+++} concentrations and different crystallographic orientations show a controllable influence of the cross-relaxation mechanism. Implications for the operation of a solid-state maser are discussed.

II. THE DEPENDENCE OF MICROWAVE SPIN SUSCEPTIBILITIES ON PUMP POWER, TEMPERATURE, AND CROSS-RELAXATION

A complete description of the magnetic properties of a system of spin levels requires the use of the spin density matrix formalism.[9] When the spin-spin phase memory time T_2 is short, in particular when $\gamma H_{\text{pump}}T_2 \ll 1$, the time dependence of the diagonal elements is described by the well-known rate equations for the populations of the various spin levels. The susceptibility near the various resonant frequencies is proportional to the difference in population of the two levels defining the resonance. The rate equation for the population of the ith level can be written in the general form

$$dn_i/dt = \sum_j (-w_{ij}n_i + w_{ji}n_j) + \sum_{jkl} w_{ijkl}N^{-1} \times (n_jn_l - n_in_k) + \sum_j W_{ij}(n_j - n_i), \quad (1)$$

$N = \sum_i n_i$ is the total number of magnetic ions,

$$w_{ij} = w_{ji}\exp(-h\nu_{ij}/kT) \quad (2)$$

is the probability per unit time for a spin transition from level i to level j, separated by an energy difference $h\nu_{ij}$, under the influence of lattice vibrations at a temperature T.

$$W_{ij} = W_{ji} = \tfrac{1}{4}\hbar^{-2}|M_{ij}|^2H_{ij}^2g(\nu_{ij}), \quad (3)$$

is the transition probability per unit time induced by pump power applied at the frequency ν_{ij}, M_{ij} is the matrix element of the component of the magnetic moment operator parallel to $H(\nu_{ij})$, $g(\nu_{ij})$ is the normalized shape function of the resonance absorption line.

The imaginary part of the susceptibility near a resonant frequency may be derived by equating the power absorbed to $\tfrac{1}{2}\omega\chi''H^2$.

$$\chi''(\nu_{ij}) = \tfrac{1}{4}\hbar^{-1}|M_{ij}|^2g(\nu_{ij})\Delta n_{ij}, \quad (4)$$

where $\Delta n_{ij} = n_i - n_j$ is the difference in population between the lower and upper levels.

w_{ijkl} is the probability per unit time for a cross-relaxation process in which one ion makes the transition $i \rightarrow j$ and simultaneously a neighboring spin the transition $k \rightarrow l$. This process is only of importance if the difference in energy $h(\nu_{ij} - \nu_{kl})$ is very small and can be taken up by the dipolar interaction of the spin

---

† The research reported in this paper was made possible through support extended Cruft Laboratory, Harvard University, by the National Security Agency. It was performed in partial fulfillment of the requirements of the Ph.D. degree at Harvard University by S. S.

* Present address: Arthur D. Little, Inc., 15 Acorn Park, Cambridge, Massachusetts.

[1] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., New York, 1947).

[2] A. H. Eschenfelder and R. T. Weidner, Phys. Rev. **92**, 869 (1953).

[3] Giordmaine, Alsop, Nash, and Townes, Phys. Rev. **109**, 302 (1958).

[4] Davis, Strandberg, and Kyhl, Phys. Rev. **111**, 1268 (1958).

[5] K. D. Bowers and W. B. Mims, Phys. Rev. **115**, 285 (1959).

[6] N. Bloembergen, Phys. Rev. **104**, 324 (1956).

[7] Scovil, Feher, and Seidel, Phys. Rev. **105**, 762 (1957).

[8] Bloembergen, Shapiro, Pershan, and Artman, Phys. Rev. **114**, 445 (1959). This paper will henceforth be referred to as BSPA.

[9] A. M. Clogston, J. Phys. Chem. Solids **4**, 271 (1958).

assembly, as discussed in BSPA. It is permissible to put the exponential factor $\exp[-h(\nu_{ij}-\nu_{kl})/kT_s]$ equal to unity in this term. The introduction of cross-relaxation terms is meaningful, when the resonances at ν_{ij} and ν_{kl} are close but well resolved. The cross-relaxation time is usually shorter than the spin-lattice relaxation time ($w_{ijkl}>w_{ij}$), if the resonances at ν_{ij} and ν_{kl} are separated by two to five times the dipolar interaction. The cross-relaxation terms are usually completely negligible for larger separations, so that frequently only one or two of the w_{ijkl} have to be considered.

It should be mentioned that spin-lattice relaxation processes may also involve transitions of two spins, the balance of energy being taken up by the lattice. This occurs if the dipolar interaction between two spins is modulated by the lattice vibrations. In this case spin-lattice relaxation terms quadratic in the occupation numbers occur. In practice the dominant spin-lattice relaxation will occur via the orbital modulation and spin-orbit coupling of individual ions. Therefore no confusion should arise by reserving the w_{ijkl} exclusively for the cross-relaxation terms.

The rate Eq. (1) may be linearized in the high-temperature approximation, when the differences in population are small, $\Delta n_{ij}\ll N$. By expanding the Boltzmann factor in Eq. (2) and omitting terms of order $(\Delta n_{ij})^2$ in Eq. (1), a set of linear equations in Δn_{ij} is obtained. The steady-state solution may readily be written in a determinantal form.[10] The dependence of the susceptibility on the pumping power at the frequency ν_{kl} takes the general form

$$\chi_{ij}''(H_{kl}^2)-\chi_{ij}''(\infty)=[\chi_{ij}''(0)-\chi_{ij}''(\infty)]\times[1+C_{kl}H_{kl}^2]^{-1}. \quad (5)$$

This equation remains valid in the presence of cross-relaxation and pumping power at other frequencies. The constant C_{kl} is a function of all other pump powers and all relaxation parameters w. For the transition kl, Eq. (7) reduces to the usual self-saturation curve with asymptotic value $\chi_{kl}''(\infty)=0$.

When all w's have the same temperature dependence $f(T)$, then $C_{kl}\propto f^{-1}(T)$ and $\chi_{ij}''(\infty)$ has the same temperature dependence as $\chi_{ij}''(0)$, i.e., Curie's law is obeyed.

This situation is expected to occur at very high temperatures, where all $w_{ij}\propto T^2$ because of Raman phonon processes, and at very low temperatures, where all $w_{ij}\propto T$ because of single phonon processes, with the important proviso that temperature-independent cross-relaxation is negligible. If cross-relaxation terms are not small compared to the spin-lattice terms, the temperature dependence of $\chi_{ij}''(\infty)$ is complex and may even decrease with decreasing temperature. In particular, lowering of the lattice temperature T may result in the transition from a regime where $w_{ij}>w_{ijkl}$ to one where $w_{ijkl}>w_{ij}$.

These general considerations are now applied to the particular case of the four spin levels of a Cr^{+++} ion, corresponding to the situation encountered in the experiments described in the following sections. It is assumed that only the ν_{24} resonance is pumped and that the level spacings and line widths are such that only the cross-relaxation between the resonances ν_{12} and ν_{23} need be considered. In addition to the six w_{ij}'s, only W_{24} and w_{1232} have to be considered. The steady state solution for the population differences is given for two special cases.

(a) Complete saturation, no cross-relaxation, $W_{24}\gg w_{ij}$, $w_{1232}=0$.

$$\Delta n_{24}=0,$$

$$\Delta n_{23}=-\frac{Nh}{4kT}\left(\frac{(w_{12}+w_{13}+w_{14})(w_{34}\nu_{34}-w_{23}\nu_{23})+w_{13}(w_{14}\nu_{34}-w_{12}\nu_{23})}{(w_{12}+w_{13}+w_{14})(w_{34}+w_{23})+w_{13}(w_{12}+w_{14})}\right). \quad (6)$$

This transition can be emissive. If the relaxation form level 3 to level 1 is negligible, $w_{13}=0$, the condition for maser action is the same as for a simple three-level system,[6] $w_{34}\nu_{34}>w_{32}\nu_{32}$.

$$\Delta n_{12}=\frac{Nh}{4kT}\left(\frac{w_{13}(w_{34}\nu_{14}+w_{23}\nu_{12})+(w_{23}+w_{34}+w_{13})(w_{14}\nu_{14}+w_{12}\nu_{12})}{(w_{12}+w_{13}+w_{14})(w_{34}+w_{23})+w_{13}(w_{12}+w_{14})}\right).$$

The resonance at ν_{12} never becomes emissive.

(b) Complete saturation, rapid cross-relaxation, $W_{24}>w_{1232}\gg w_{ij}$.

$$\Delta n_{24}=0,$$

$$\Delta n_{12}=\Delta n_{23}$$

$$=+\frac{Nh}{4kT}\left\{\frac{2w_{13}\nu_{13}+w_{12}\nu_{12}+w_{23}\nu_{23}+w_{14}\nu_{14}-w_{34}\nu_{34}}{w_{12}+4w_{13}+w_{14}+w_{23}+w_{34}}\right\}. \quad (7)$$

In this case both resonances ν_{12} and ν_{23} may become emissive when

$$w_{34}\nu_{34}>2w_{13}\nu_{13}+w_{12}\nu_{12}+w_{23}\nu_{23}+w_{14}\nu_{14}. \quad (8)$$

This condition is more difficult to satisfy than the condition that (6) be negative. On the other hand, if because of cross-saturation Δn_{23} becomes positive, $\Delta n_{34}=-\Delta n_{23}$ will surely be negative. The action of the transition ν_{12} is similar to the action of the transition

---

[10] J. P. Lloyd and G. E. Pake, Phys. Rev. **94**, 579 (1954).

in another ionic species at the same frequency. Scovil[11] *et al.* describe such an influence of Ce^{+++} on the population of the Gd^{+++} levels in a mixed crystal.

Finally, it should be emphasized that Eq. (1) does not include the most general form of cross-relaxation. As pointed out in BSPA, processes in which more than two transitions take place simultaneously are possible. One then has third-order transition probabilities w_{ijklmn}, which are not negligible if $\nu_{ij}+\nu_{kl}+\nu_{mn}$ is zero or comparable with the dipolar interactions. The cubic terms in the rate equations can again be linearized in the population differences Δn in the high-temperature approximation. Fourth-order terms with $w_{ijklmnop}$ can be introduced in a similar fashion and have been used in BSPA to explain cross-saturation effects in copper tutton salt.

III. EXPERIMENTAL METHOD

Crystals of $K_3(CoCr)(CN)_6$ were grown from aqueous solution by controlled evaporation. The relative $[Cr^{+++}]$ concentration in the solution was 0.5% and 2%. Small single crystals were placed in a maser-type cavity of a design described previously.[12] A small size of crystal is chosen since the purpose is to obtain reliable values for the microwave susceptibilities. Heavy loading of the cavity, useful in maser operation, is avoided. The field intensity over the sample at both microwave frequencies was uniform to within 5%.

The cavity was tunable at *X* band by a movable diaphragm coupling which could slide with quarter-wave sections in standard *X*-band guide. The *X*-band pump power was supplied by a Varian *V*-58 klystron. *L*-band signal power was supplied by a 5981 klystron or a Navy Model LAG signal generator run from an external power supply. Although *L*-band tuning by capacitive loading of the quarter-wavelength resonator proved feasible, the present experiments were carried out at a few fixed *L*-band frequencies with fixed resonators.

The klystrons at both frequencies were locked to the sample cavity resonance with a repeller voltage modulation feedback system similar to that developed by Kip.[13] Influence of the dispersive components of the susceptibility was eliminated.

A rotatable electromagnet supplied the dc magnetic field. In the present experiments the crystals were oriented in such a way that the magnetic field could rotate in the *ac* plane. In this plane the two ions in the unit cell are magnetically equivalent, so that only four energy levels have to be considered. The variation of the splittings ν_{12}, ν_{23} and ν_{24} is plotted in Fig. 1 as a function of the magnitude of the magnetic field H_0 for various angles θ between the *a* axis and $\mathbf{H}_0$ in the *ac* plane. The curves have been calculated from published tables for the energy levels.[14] It is seen that the resonances ν_{12} and ν_{23} coincide for $\theta=0$ at about 1700 Mc/sec, but can be made to deviate considerably at other angles at the same frequency. As the angle θ is varied, the value of H_0 is adjusted to keep ν_{23} at the indicated *L*-band frequency. The *X*-band resonant frequency ν_{24} does not vary too much under these conditions. Pumping at ν_{24} remains possible. Calculation of the other resonant frequencies ν_{13}, ν_{14}, and ν_{34} shows that these resonances remain all well separated from each other and the other resonances. It is thus possible to create an experimental situation in which only one cross-relaxation process w_{1232} with variable strength is of importance.

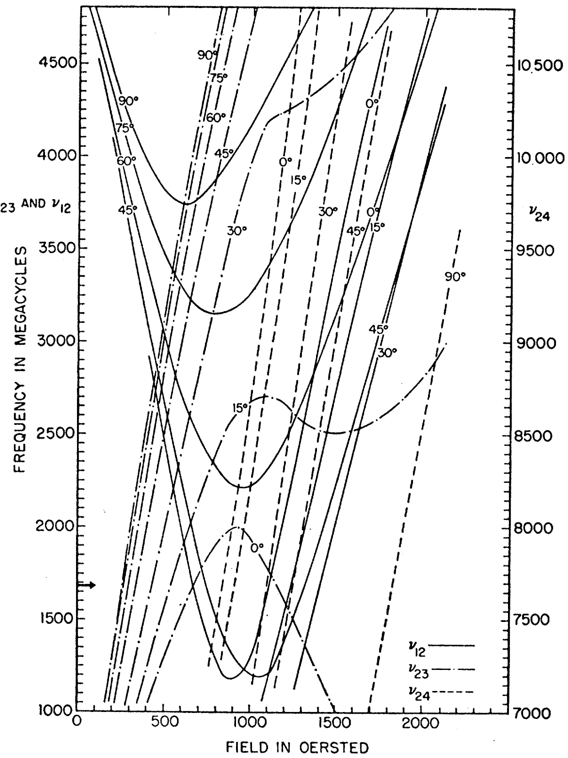

FIG. 1. The resonant frequencies ν_{12}, ν_{23}, and ν_{24} between the four levels of Cr^{+++} in $K_3(CoCr)(CN)_6$ as a function of the magnetic field strength H_0 in the crystallographic ac plane, for different angles between H_0 and the *a* axis. The graph was calculated from published tables for the energy levels.[14] The arrow indicates the *L*-band operating frequency.

Incident power at both frequencies can be monitored with the aid of directional couplers and thermistors. The reflected power at *L* band is modulated at 15 cps by modulation of the dc magnetic field, and it is displayed after rectification by a 1*N*21*C* crystal on an

---

[11] Schulz-duBois, Scovil, and de Grasse, Bell System Tech. J. **38**, 335 (1959).

[12] Artman, Bloembergen, and Shapiro, Phys. Rev. **109**, 1392 (1958). A detailed description of the experimental aspects may be found in the thesis by Sidney Shapiro, Harvard University, May, 1959.

[13] A. F. Kip (private communication).

[14] W. S. Chang and A. E. Siegman, Technical Report No. 156–1 for $K_3(CoCr)(CN)_6$, Stanford Electronics Laboratories, Stanford University (unpublished).

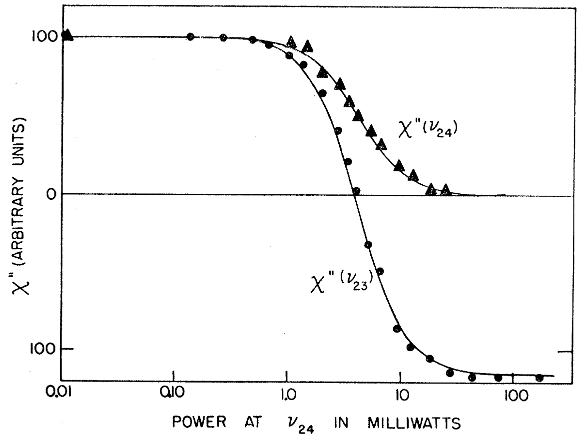

FIG. 2. The susceptibility χ'' at the frequencies ν_{23} and ν_{24}, respectively, as a function of pump power applied at ν_{24}. The crystal $K_3(0.995\text{ Co}, 0.005\text{ Cr})(CN)_6$ was maintained at 2.5°K. The magnetic field $H_0=1175$ oersteds makes an angle $\theta=10°$ with the *a* axis in the *ac* plane. The drawn curves have the theoretical form of Eq. (5). The final spin temperature $T_f=-2.2$°K at ν_{23} and $T_f=\infty$ at ν_{24}.

oscilloscope or after passage through a narrow-band receiver on a pen recorder. The coaxial line contains a low-pass filter to eliminate X-band power. The L-band susceptibility is measured as a function of X-band pump power. Self-saturation curves at X-band are taken by measuring the reflected power in the X-band guide in a similar manner. With the small samples used the reduction from change in reflected power to change in susceptibility of the sample is straightforward. The power at L band was sufficiently low that saturation at the signal frequency was negligible, $W_{23}\ll w_{ij}$.

IV. EXPERIMENTAL RESULTS

The general dependence of the susceptibilities on pump power is illustrated in Fig. 2. The drawn curves have the theoretical form of Eq. (5). The experimental points of both the L-band and the X-band susceptibility (self-saturation) are in good agreement[15] with the theory of Sec. III.

Strandberg[16] has pointed out that considerable deviations from Eq. (5) should be expected if the phonon-bath contact were a bottleneck rather than the spin-lattice relaxation. The extent of phonon-heating and the heat conductivity would change with pump power. There is apparently no experimental evidence for this.

The rather large negative asymptotic value for the L-band susceptibility indicates the suitability of this material for maser operation. In early papers on masers[17] graphs of gain *vs* pump power did not show any indica-indication for such an asymptotic behavior. The explanation for the shape of those gain-*vs*-pump power curves, which have no fundamental significance, can be based on the following two reasons. As χ'' approached its asymptotic value, $\chi''(\infty)$, the maser approached the point of instability *versus* oscillation due to the choice of external coupling of the maser cavity. In the second place, the pump field intensity was not uniform over the sample. As the pump power increased, successively larger regions of the crystal became emissive.

There will still be an asymptotic value for the effective susceptibility at high pump power level. The approach to this limiting value will be more gradual than the curves in Fig. 2. The detailed shape depends on the field configurations at both the pump and the maser frequency in the cavity. Since the effects of spatial spin diffusion in the nonuniformly saturated crystal is negligible, the effective susceptibility at ν_{ij}, including the filling factor, as a function of pump power at ν_{kl} is given by

$$4\chi_{ij,\,\mathrm{eff}}''(H_{kl}^2)\underset{\text{cavity}}{\iiint}\sum_{\alpha}\left[(H_{ij}^{\alpha})^2/8\pi\right]dV$$

$$\doteq\hbar^{-1}g(\nu_{ij})\left[\Delta n_{ij}(0)-\Delta n_{ij}(\infty)\right]$$

$$\times\underset{\text{sample}}{\iiint}\frac{(\sum_\alpha M_{ij}^{\alpha}H_{ij}^{\alpha})^2dV}{1+C_{kl}'(\sum_\alpha M_{kl}^{\alpha}H_{kl}^{\alpha})^2}$$

$$+\hbar^{-1}g(\nu_{ij})\Delta n_{ij}(\infty)\underset{\text{sample}}{\iiint}(\sum_{\alpha}M_{ij}^{\alpha}H_{ij}^{\alpha})^2dV. \qquad (9)$$

The summation α is over the three Cartesian coordinates. H_{ij}^{α} and H_{kl}^{α} are functions of position in the cavity. $\Delta n_{ij}(0)$ and $\Delta n_{ij}(\infty)$ are the differences in population of levels i and j in thermal equilibrium and at infinite pumping power at the frequency ν_{kl}. These quantities as well as C_{kl}' are not a function of position.

The approach of χ''(eff) to an asymptotic value is important for maser operation. It implies a good stability against amplitude and frequency fluctuations in pump power[18] which is not shared by certain parametric amplifiers.

In Fig. 3 data for the temperature dependence of the asymptotic value $\chi''(\infty)$ are shown. Instead of $\chi''(\infty)$ a final spin temperature T_f defined by

$$T_f=T\Delta n_{23}(0)/\Delta n_{23}(\infty)=T\chi''(0)/\chi''(\infty),$$

is plotted. Clearly, $\chi''(\infty)$ is proportional to $\chi''(0)$ or inversely proportional to T. Curie's law is valid.

The power required to reach the value halfway

---

[15] The pump power scale in Fig. 8 of BSPA does not match with the scales of Figs. 9–11. This is due to an error in calibration, which was eliminated in taking the data presented here. The calibration error does not impair the argument in BSPA, which is only concerned with the relative displacements of the two self-saturation curves in Fig. 8.

[16] M. W. P. Strandberg, Phys. Rev. **110**, 65 (1958).

[17] A. L. McWhorter and J. W. Meyer, Phys. Rev. **109**, 312 (1958).

[18] Giordmaine, Alsop, Nash, and Townes, Proc. Inst. Radio Engrs. **47**, 1062 (1959).

between $\chi''(0)$ and $\chi''(\infty)$ is proportional to the absolute temperature. These data are therefore consistent with the explanation that all w_{ij} are determined by single phonon processes and are all proportional to T, whereas cross-relaxation terms are absent for the crystalline orientation used ($\theta=30°$). This result is in agreement with the data of Eschenfelder[2] on Cr^{+++} in an alum.

As explained in Sec. II, cross-relaxation should become important, when the angle θ approaches zero, as $\nu_{12}=\nu_{23}$ for $\theta=0°$. In Fig. 4 $\chi''(\infty)$ is shown as a function of $\nu_{12}-\nu_{23}$ at two different concentrations. The result of cross-relaxation is that maser action is suppressed, $\chi''(\infty)\geqslant 0$. This occurs at small values of θ and at high magnetic concentration for all values of θ.

This result is physically understandable because one has to compete with various relaxation mechanisms to and from level 1, if cross-relaxation w_{1232} is important. This is expressed mathematically by Eqs. (6) and (7). Apparently the condition (8) is not satisfied. At $\theta=0$ one measures, of course, not χ_{23}'', but $\chi_{23}''+\chi_{12}''$. This does not change the argument for the ratio

$$\frac{\chi_{12}''(\infty)+\chi_{23}''(\infty)}{\chi_{12}''(0)+\chi_{23}''(0)}=\frac{T_f}{T},$$

since the susceptibilities of the two transitions are described by the same temperature because of the coincidence of the resonant frequencies.

The difference in T_f at 1000 and 3000 Mc/sec separation is probably caused by the variation of the matrix elements $M_{ij}(\theta)$ and the consequent variation in the ratio of the $w_{ij}(\theta)$ at $\theta=14°$ and $\theta=32°$, respectively. The matrix elements[14] do not change much for $\theta\sim 10°$, and the rapid change in T_f in this region is caused by the onset of cross-relaxation. One may crudely estimate that w_{1232} becomes of the same order as the w_{ij} ($\sim 10^{+3}$ sec^{-1}) at separation $\nu_{12}-\nu_{23}=400$ Mc/sec. In the more concentrated sample cross-relaxation is important at all separations.

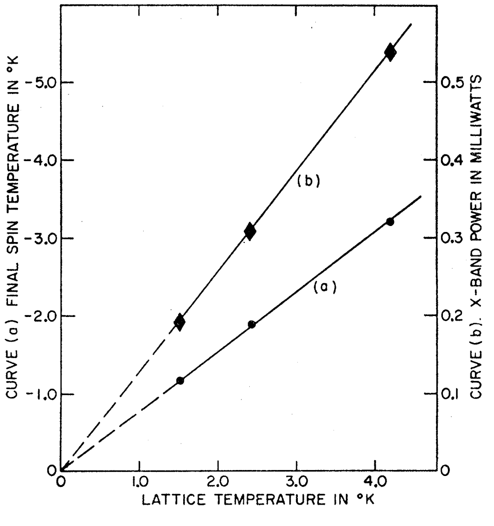

FIG. 3. Curve (a). The final spin temperature $T_f=T\chi''(0)/\chi''(\infty)$ at ν_{23} as a function of the lattice temperature. Curve (b). The pump power at ν_{24} required to produce 50% saturation at ν_{23}, i.e., to obtain a value $\chi''=\frac{1}{2}[\chi''(0)+\chi''(\infty)]$, as a function of the lattice temperature. The magnetic field $H_0=1390$ oersteds in the ac plane makes an angle $\theta=30°$ with the a axis of the crystal $K_3(0.995\ Co, 0.005Cr)(CN)_6$.

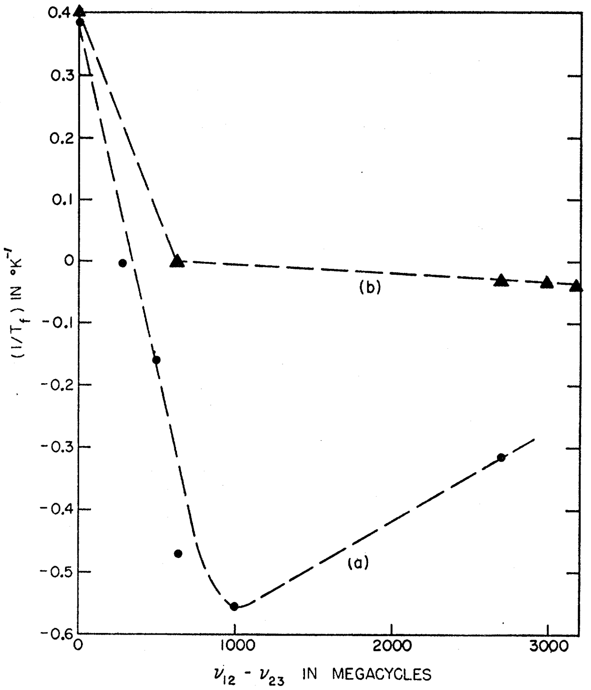

FIG. 4. The inverse of the final spin temperature $T_f^{-1}\propto\chi''(\infty)$ is plotted as a function of the separation between the resonances at ν_{12} and ν_{23}. The separation $\nu_{12}-\nu_{23}=1000$ Mc/sec corresponds to $\theta=14°$. The magnetic field is varied in the ac plane of $K_3(CoCr)(CN)_6$ in magnitude and direction so as to keep $\nu_{23}\approx 1700$ Mc/sec. Curve (a) is for 0.5% Cr^{+++} concentration, curve (b) is for 2% Cr^{+++} concentration. Cross-relaxation effects are important near zero separation at the lower concentration and at all separations at the higher concentration.

The marked concentration dependence of T_f because of the onset of cross-saturation provides the clue for the action of light ruby as an amplifier and dark ruby as an attenuator in the same traveling-wave maser.[19]

Another interesting observation has been made about the temperature dependence of $\chi_{23}''(\infty)$ at $\nu_{12}-\nu_{23}=600$ Mc/sec. Cross-relaxation in this orientation is comparable with spin-lattice relaxation at 4.2°K according to Fig. 4. When the crystal is cooled and the w_{ij} become smaller, cross-relaxation should become dominant. It was indeed observed that lowering the temperature T caused an increase in $|T_f|$. In other words, maser action became poorer at the lower temperature. Cross-relaxation provides a natural explanation for this

---

[19] DeGrasse, Schulz-du Bois, and Scovil, Bell. System Tech. J. 38, 305 (1959).

effect, which has a reverse trend from the usual Curie behavior shown in Fig. 3.

The magnitude of w_{1232} may be estimated theoretically from an approximate formula given by BSPA,

$$w_{1232}=(2\pi)^{-\frac{1}{2}}\hbar^{-2}|\mathcal{H}_{1232}|^2(\Delta\nu_{12}^2+\Delta\nu_{23}^2)^{-\frac{1}{2}} \times\exp[-(\nu_{12}-\nu_{23})^2/2(\Delta\nu_{12}^2+\Delta\nu_{23}^2)]. \quad (10)$$

The resonant lines at ν_{12} and ν_{23} are assumed to have a Gaussian shape with second moments

$$\Delta\nu_{12}^2 \quad \text{and} \quad \Delta\nu_{23}^2,$$

respectively, due to the dipolar interaction between neighboring Cr^{+++} ions, $\mathcal{H}_{1232}$ is the matrix element of the dipolar interaction of Cr^{+++} and its neighbors responsible for the double transition.

The second moments may be estimated from the observed line shape at the two resonances, if the contribution of the nuclear spins is subtracted. The calculated second moments $(\Delta H)^2$ of the local fields may be converted to a frequency scale by multiplication with $(\partial\nu/\partial H)^2$, evaluated at the appropriate resonant frequency. In this way the values $(\Delta\nu_{12}^2+\Delta\nu_{23}^2)^{\frac{1}{2}}=115$ Mc/sec and 350 Mc/sec for 0.5% and 2% Cr^{+++} concentration are found. It should be remembered that these are the nominal concentrations in the solution and the concentration in the crystals may be different. Since the local field from the Cr^{+++} ions is comparable or larger than the field arising from the nuclear spins, the use of Eq. (10) is justifiable. For the average value of $\hbar^{-2}|\mathcal{H}_{1232}|^2$ one may take approximately $0.1(\Delta\nu_{12}^2+\Delta\nu_{23}^2)$. In this way w_{1232} at a separation $\nu_{12}-\nu_{23}=400$ Mc/sec is estimated to be 10^{+4} sec^{-1}, in the crystal at 0.5% concentration. At $\nu_{12}-\nu_{23}=1000$ Mc/sec, $w_{1232}=10^{-10}$ sec^{-1}, which is negligibly small. The intricacies of cross-relaxation in dilute magnetic materials have not been considered in detail, but it is gratifying that a reasonable order of magnitude for the onset of cross-relaxation is obtained.

For the crystal with the higher concentration, at 1500 Mc/sec separation, the estimate $w_{1232}=10^{+3}$ sec^{-1} is made. The Gaussian function would give negligible cross-relaxation at 3000 Mc/sec. The tail of the resonances is probably not adequately represented by the Gaussian function (10) and no detailed explanation is offered for the constancy of T_f over a wide range of separations.

The fact that the two samples with different concentration give the same result for $\theta=0°$ is gratifying. Here there is complete overlap and the cross-relaxation is always very short $w_{1232}\gg w_{ij}$. Equation (7) should be valid in this case at all concentrations and a result independent of concentration is obtained. The term in w_{1232} is essential to explain both curves of Fig. 4, because it is inconceivable that the ratios of the w_{ij}'s would have a strong mixed dependence on concentration and orientation.

Extrapolation of the data presented here shows why undiluted magnetic salts are unsuitable for maser operation in the conventional microwave region although not necessarily at higher frequencies. There will always be sufficient overlap of resonances in the whole system of spin levels to reach internal thermal equilibrium, as proposed by Casimir and du Pré.[20] When such a system is pumped at any frequency, the system will warm up as a unit to infinite temperature. Validity of the Casimir-du Pré hypothesis of thermodynamic equilibrium and maser operation are mutually exclusive.

The bandwidth of a maser at gain unity cannot be increased, by increasing the magnetic concentration, beyond a certain limit of approximately one third the distance between adjacent resonances. This limitation can be circumvented by loading the maser with a number of single crystals in slightly different orientations.[19]

---

[20] H. B. G. Casimir and F. K. du Pré, Physica **5**, 507 (1938).