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CROSS-DOPING AGENTS FOR RUTILE MASERS
(6th quarter)

P. F. Chester

Westinghouse Research Laboratories
Pittsburgh 35, Pennsylvania

Research Report 403FD449-R6

Contract AF 19(604)5589, Task 46210, Project 4156

September 1960

Prepared for

ELECTRONICS RESEARCH DIRECTORATE
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
AIR FORCE RESEARCH DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
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CROSS-DOPING AGENTS FOR RUTILE MASERS*

P. F. Chester**

Abstract

Tantalum and niobium appear to be suitable cross-doping agents for securing a short spin-lattice relaxation time in masers using rutile as the host crystal. Initial tests on rutile doped with chromium and tantalum are encouraging. Cerium does not appear to enter rutile as Cr^{3+}. Departure from stoichiometry, although it results in a spectrum with short spin-lattice relaxation time, presents the problem of non-frequency-selective cross-relaxation.

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*This text is as submitted for publication in the Journal of Applied Physics.

**Present address: Central Electricity Research Laboratories, Leatherhead, Surrey, ENGLAND.

INTRODUCTION

In the three-level maser[1] and in proposals for four-level[2,3] and continuously operating two-level masers,[4] it is desired to decrease the spin lattice relaxation time, T_1, between a given pair of spin states. One method of achieving this is to "cross-dope" the host crystal with a second paramagnetic ion having a short T_1 and a transition degenerate with the appropriate transition of the maser ion.[5,6,7] In view of the

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1. N. Bloembergen, Phys. Rev. 104, 324 (1956).
2. G. Makhov, Bull. Am. Phys. Soc., 4, 21 (1959).
3. P. E. Wagner, Westinghouse Research Report 403FF200-R1, May, 1959.
4. D. I. Bolef and P. F. Chester, IRE Trans. MTT-6, 47 (1958).
5. G. Feher and H.E.D. Scovil, Phys. Rev. 105, 760 (1957).
6. E. O. Schulz-duBois, H.E.D. Scovil, and R. W. DeGrasse, Bell System Technical Journal 38, 335 (1958).
7. J. M. Minkowski, Phys. Rev. 119, 1577 (1960).

importance of chromium and iron doped rutile as maser materials, cross-doping agents for rutile are of interest, The present paper describes some results obtained with tantalum, niobium, and cerium doping and also with departures from stoichiometry. The measurements were made using a reflection type superheterodyne spectrometer operating near 9 KMc/s in the temperature range from 1.5°K to 50°K.

NIOBIUM DOPING

The EPR spectrum of a carefully oxidized sample* of niobium doped rutile was examined at 4.2°K. It is interpreted as due to Nb^{4+} ($S = 1/2$; Nb^{93}, 100 per cent abundant, $I = 9/2$) substituting for Ti^{4+} with two sites per unit cell. The spin Hamiltonian appropriate to this case is[8,9]

$$\mathcal{H} = \beta(g_z H_z S_z + g_x H_x S_x + g_y H_y S_y) + A_z S_z I_z + A_x S_x I_x + A_y S_y I_y + \frac{3}{2} P_z \left[I_z^2 - \frac{1}{3} I(I+1) \right] + \frac{P_x - P_y}{2} (I_x^2 - I_y^2) - g_n \beta_n \underline{H} \cdot \underline{I}$$

With H // 110 and H // c, the spacing of the hyperfine lines was regular within the resolution of the experiment. The terms involving P were therefore neglected in obtaining the principal values of g and A given in Table I.

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*Grown by flame fusion at M.I.T. and kindly loaned to the author by Dr. H.P.R. Frederikse.

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8. K. D. Bowers and J. Owen, Reports on Progress in Physics, 18, 304 (1955).

9. B. Bleaney, K. D. Bowers and D.J.E. Ingram, Proc. Roy. Soc. A228, 147 (1955).

TABLE I

Direction of H	g	A x 10^4 cm^{-1}
c	1.948	2.1
110	1.981	8.0
$1\bar{1}0$	1.973	$\leq$ 1.8

In the $1\bar{1}0$ direction the hyperfine structure was not resolvable. With H // c the overall width of the pattern was $\sim$ 25 gauss, while with H // 110 it was $\sim$ 90 gauss. When the magnetic field was not along a principal axis, a set of nine lines was observed in between the ten hyperfine lines. These are attributed to normally forbidden transitions, ($\Delta m_n = \pm 1$), allowed because of the Nb quadrupole interaction. Similar lines have been seen in the resonance of Cu^{2+} by Bleaney et al.[9]

The main features of the present spectrum were observed to remain unchanged up to about 25°K. Above this temperature, the hyperfine structure gradually disappeared and the line narrowed and became dispersive. At the same time the microwave coupling was observed to change markedly. This behavior is attributed to the onset of electronic conduction.

An attempt was made to measure T_1 by the field sweep inversion method[10] at 1,4°K. The line could not be inverted and the relaxation time appeared to be about 70 μsec. Thus, with H not too far from the c axis (to keep down the overall width of the spectrum) niobium should be a satisfactory cross-doping agent in rutile masers.

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10. J. G. Castle, P. F. Chester, and P. E. Wagner, Phys. Rev. 119, 953 (1960).

TANTALUM DOPING

The tantalum doped rutile, nominally 0.05 atomic per cent Ta, was grown by the National Lead Company. A sample cut straight from the boule and a sample oxidized in a stream of oxygen at 750°C for six hours showed identical spectra, which are interpreted as due to Ta^{4+} (S = 1/2; Ta^{181}, 100 per cent abundant, I = 9/2) substituting for Ti^{4+}. The spin Hamiltonian is the same as that for Niobium. In the case of Tantalum, however, the hyperfine structure was only resolvable with H // c and the effects of the Ta quadrupole moment were clearly important. Because of the poor resolution it was not possible to obtain accurate values for A and P. The values for A in Table II are only approximate.

TABLE II

Direction of H	g	A x 10^4 cm^{-1}
c	1.945	$\sim$ 2.7
110	1.979	< 2.5
$1\bar{1}0$	1.979	< 2.5

The overall width of the spectrum at any orientation was less than 35 gauss.

The main features of the spectrum were observed to remain unchanged up to about 10°K above which temperature the hyperfine structure disappeared, the line narrowed and became dispersive and the microwave coupling changed markedly. At 1.4°K the spin lattice relaxation time appeared to be about 100 μsec.

In order to test the suitability of Ta for cross-doping, experiments were carried out on two different rutile crystals doped with both chromium and tantalum. The first crystal contained nominally 0.05 atomic per cent Cr and 0.1 atomic per cent Ta. It appeared to be electrically conducting even at $2^{\circ}K$ and no relaxation data could be obtained. The second crystal contained nominally 0.05 atomic per cent Cr and 0.05 atomic per cent Ta. This appeared to be slightly lossy at $4.2^{\circ}K$ but not sufficiently to interfere with relaxation measurements. The 3-4 transition* of the Cr^{3+} ion was examined at $4.2^{\circ}K$ with H in the plane formed by the c axis and a 110 axis. The values of T_1 obtained are given in Table III, where θ is the angle between H and the 110 axis.

TABLE III

θ Degrees	H oersteds	T_1, milliseconds
0	3910	0.74
9.3	3500	0.64
10.8	3400	0.47
12.0	3305	0.16**
13.7	3200	0.59
15.3	3100	0.85

** Coincidence with the Ta line.

It may be seen that the spin lattice relaxation of the chromium line is speeded up by a factor of four or five when it is made coincident with the tantalum line. The effect does not extend much beyond $\pm$ 100 oersteds

* Numbering the energy levels in order of increasing energy.

from coincidence. The results are not completely satisfactory, however, since T_1 at $\Theta = 15.3$ is about four times shorter than in rutile doped only with chromium, probably due to the (albeit low) conductivity of the sample. Presumably this could be rectified by decreasing the Ta content or increasing the Cr content. It should also be noted that the Ta + Cr doped crystals were visibly inhomogeneous in composition.

It would seem that Tantalum is indeed a suitable cross-doping agent for Cr:TiO_2 masers but further work needs to be done on homogeneous crystals of greater Cr:Ta ratios with the actual values of H and Θ that would be used in a maser application.

CERIUM DOPING

The cerium doped rutile, nominally 0.1 atomic per cent Ce, was also grown by flame fusion.* Unlike the Nb and Ta doped crystals, it was not blue in color. No spectrum that could be attributed to Ce^{3+} was observed down to 1.4°K. Presumably the cerium is present as Ce^{4+} substituting for Ti^{4+}.

In an attempt to change the valence state of the cerium, a sample was heated in vacuum for 24 hours at 1000°C. This produced a blue coloration and two spin resonance spectra at helium temperatures. An extensive and complicated set of lines extends from $g \sim 2.05$ to $g \sim 1.73$. This spectrum is very similar to that observed in strongly reduced rutile. The second spectrum corresponds to a center with $S = 1/2$ on two sites each having the following characteristics.

*National Lead Company

Direction of H	g
c	3.86_6
110	2.06_9
$1\bar{1}0$	4.39_4

This center is tentatively identified as Ce^{3+} on a titanium site. The relaxation time at 4.2°K was found to be ~ 4 milliseconds with H // 110 and ~ 1 millisecond with H // c.

NON-STOICHIOMETRIC RUTILE

The spin resonance of slightly oxygen deficient rutile* has already been reported(11) and is characterized by a moderate relaxation time, 12 milliseconds at 2.16°K. At greater degrees of reduction, where the sample has a deep transparent blue color (in a thickness of one millimeter), the spectrum changes character and a single, motionally narrowed line is observed. The relaxation time of this line is less than 100 μsec at 2.16°K. To test the usefulness of this line for cross-doping, a sample of chromium doped rutile (nominally 0.1 atomic per cent Cr^{3+}) was subjected to varying degrees of reduction and its relaxation behavior subsequently examined.

Heating in a vacuum of 10^{-5} mm Hg for 24 hours at temperatures up to 1000°C did not introduce the motionally narrowed line but rather an untidy group of lines centered about the same g value. The relaxation time of this group appeared to be about the same as that of the Cr^{3+}, a

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*Prepared by reoxidation of 'as grown' rutile.

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11. P. F. Chester, Bull. Am. Phys. Soc. II, 5, 72 (1960).

few milliseconds at 4.2°K. Coincidence with the 1-2 line or the 3-4 line of the Cr^{3+} spectrum produced no noticeable reduction in relaxation time of the Cr^{3+} lines.

Heating a sample in hydrogen for 15 minutes at 850°C resulted in an opaque crystal with an untidy spectrum very similar to that of the vacuum reduced samples. Relaxation measurements on the "oxygen deficient" spectrum of this sample gave T_1 250 μsec at 1.4°K. However, it was found that T_1 for the 1-2 line and 3-4 line of Cr^{3+} was now about 70 μsec irrespective of proximity to the oxygen deficient spectrum. Presumably there is sufficient electronic conductivity in this sample for the relaxation to be dominated by a process involving conduction electrons. Such a process would be expected to become less effective at higher fields such that the Zeeman energy exceeded the thermal energy of the electrons. It would seem that the oxygen deficient spectrum is not as useful for cross-doping as Ta or Nb.

ACKNOWLEDGMENTS

The author wishes to thank Clinton C. Brooks and J. R. Sutter for assistance in making the measurements.

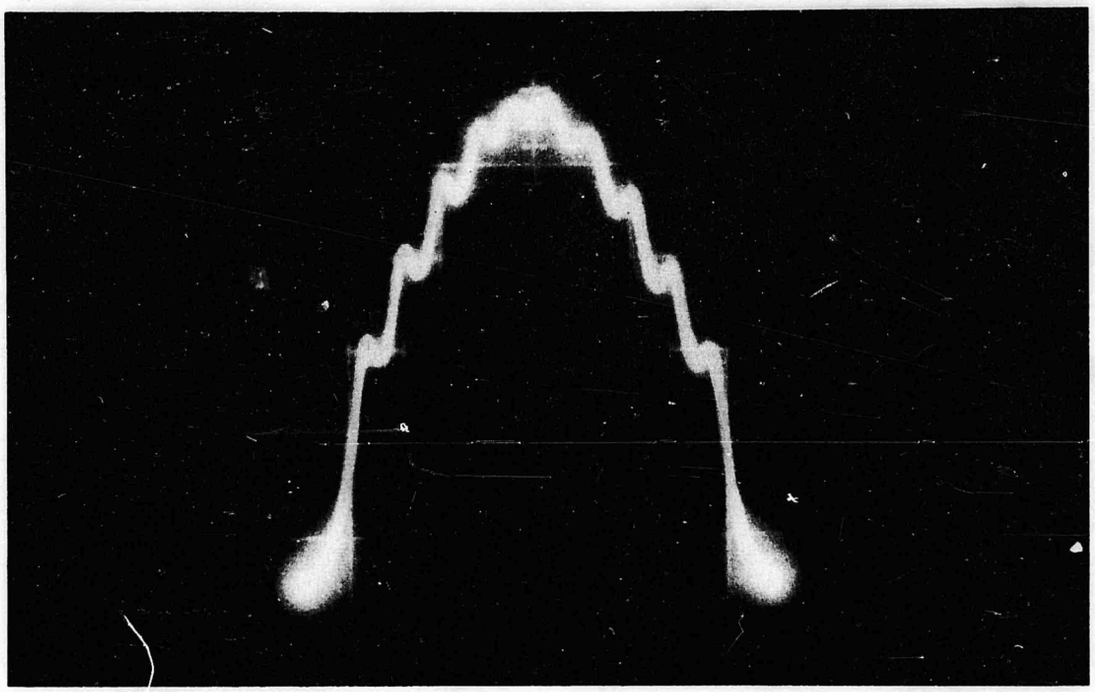

FIG. 1 - SPECTRUM OF NIOBIUM IN RUTILE AT 4.2^{o}K

Field along C axis
Sweep width 30 oersteds

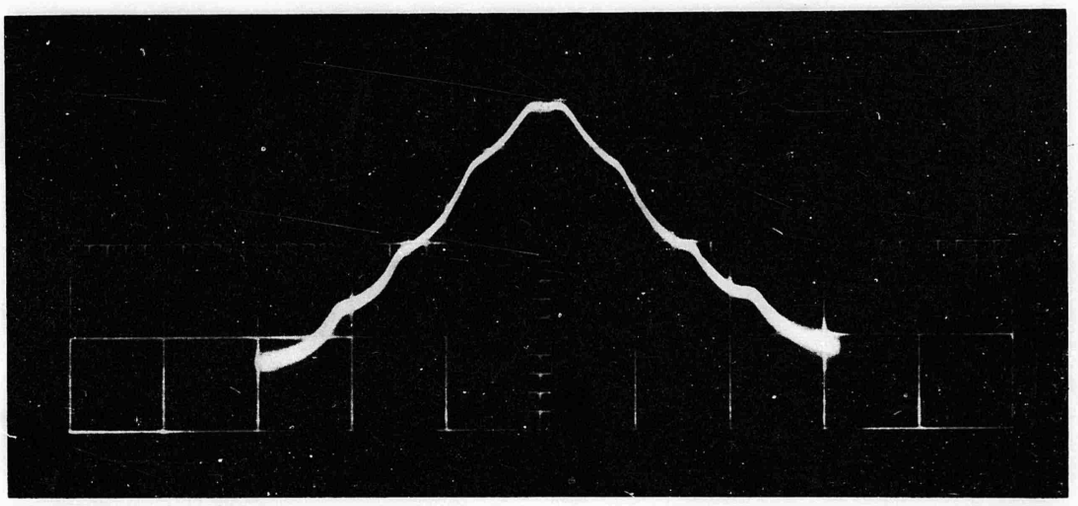

FIG. 2 - SPECTRUM OF TANTALUM IN RUTILE AT 4.2^{0}K

Field along C axis
Sweep width 30 oersteds

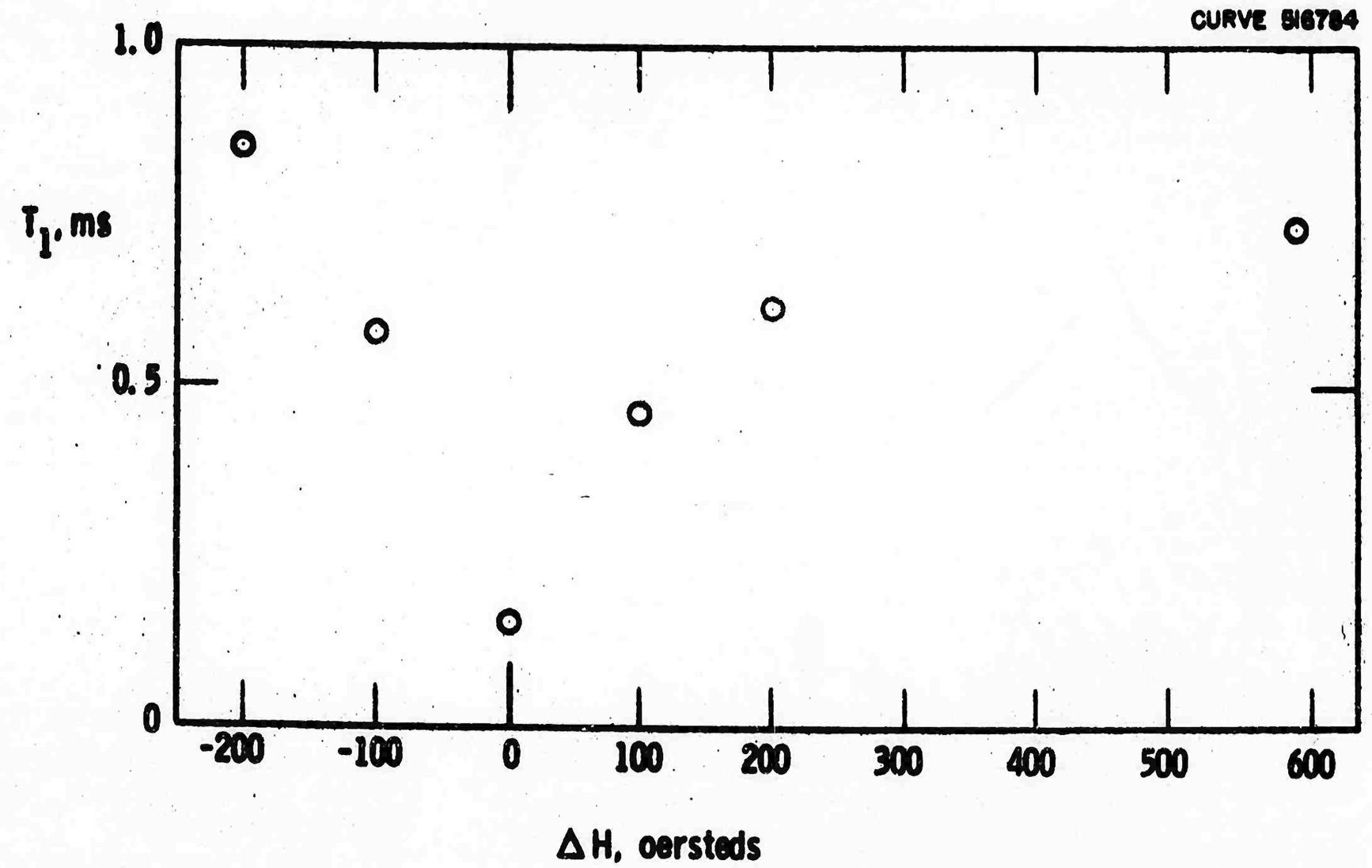

FIG. 3 - RELAXATION TIME OF CHROMIUM 3-4 LINE AS FUNCTION OF PROXIMITY TO TANTALUM LINE. TEMP. 4.2°K.