

Cross Relaxation Effect of Chromium and Iron in $K_3(\text{Co,Cr,Fe})(\text{CN})_6^\dagger$

JAN M. MINKOWSKI

Radiation Laboratory, The Johns Hopkins University, Baltimore, Maryland

(Received April 8, 1960; revised manuscript received April 28, 1960)

Strong coupling between spins of Cr^{3+} and Fe^{3+} and large ratio of spin-lattice relaxation times of these two ions at 4.2°K are demonstrated by inversion of ν_{14} transition of Cr^{3+} , when ν_{13} and ν_{24} transitions are saturated. At 1.9°K the spin-lattice relaxation times are nearly equal and no inversion takes place.

It has been known for some time¹⁻³ that in an electron-spin system with $S=3/2$ (Fig. 1) it should be possible to invert populations of the high-frequency ν_{14} transition⁴ by saturating the lower frequency transitions ν_{13} and ν_{24} . It is essential, however, that the spin-lattice relaxation time of the ν_{23} transition be sufficiently shorter than the spin-lattice relaxation times of the other spin transitions. In Makhov's¹ unsuccessful attempt to invert the ν_{14} line in ruby, this last condition apparently was not satisfied.

We have inverted the ν_{14} transition of Cr^{3+} ion in diluted $K_3\text{Cr}(\text{CN})_6$ by saturating the ν_{13} and ν_{24} transitions and by increasing the rate of transfer of energy from ν_{23} transition to the lattice. As in the experiment of Feher and Scovil⁵ another ion, in our case Fe^{3+} , was added to the crystal. The method depends on strong cross relaxation^{6,7} between two spin species. When the frequency of the iron line⁸ coincides with ν_{23} , the transfer of excitation from Cr^{3+} to Fe^{3+} occurs in times of the order of 3×10^{-8} sec. At the temperature of liquid helium this is several orders of magnitude faster than spin-lattice relaxation times of either ion [$T_1(\text{Cr}), T_1(\text{Fe})$]. With equal concentrations of the two paramagnetic ions and if

$$T_1(\text{Cr})/T_1(\text{Fe}) \gg 1 \quad (1)$$

the spin temperature of the ν_{23} transition is determined

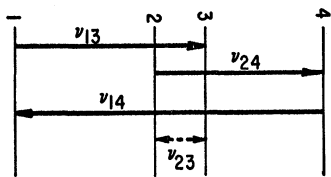


FIG. 1. Schematic diagram of energy levels of an ion with $S=3/2$. To invert populations of ν_{14} line by saturating ν_{13} and ν_{24} lines, condition $T_1^{23} \ll T_1^{14}$ must be satisfied.

[†] This research was supported by the Air Research and Development Command, Wright Air Development Division.

¹ G. Makhov, *Bull. Am. Phys. Soc.* **4**, 21 (1959).

² P. E. Wagner, Westinghouse Research Laboratories Report 403FF200-R1, 1959 (unpublished).

³ J. M. Minkowski, The Johns Hopkins University, Radiation Laboratory, Report AF-73, III, 1959 (unpublished).

⁴ Notation follows N. Bloembergen, *Phys. Rev.* **104**, 324 (1956).

⁵ G. Feher and H. E. D. Scovil, *Phys. Rev.* **105**, 760 (1957).

⁶ N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, *Phys. Rev.* **114**, 445 (1959).

⁷ S. Shapiro and N. Bloembergen, *Phys. Rev.* **116**, 1453 (1959).

⁸ K. D. Bleaney and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 345.

by $T_1(\text{Fe})$ and is equal to the temperature of the lattice. The difference of populations of the levels 2 and 3 of Cr^{3+} is then, $n_2 - n_3 = n_2^0 - n_3^0 = (Nh/4kT)\nu_{23}$, where n_2^0 , n_3^0 are spin populations at equilibrium and where we have assumed $h\nu_{23}/kT \ll 1$. Since the transitions ν_{13} and ν_{24} are saturated we also have, $n_1 = n_3$ and $n_2 = n_4$. The last three equations determine the inversion of the populations of the levels 1 and 4, $n_1 - n_4 = -(Nh/4kT)\nu_{23}$. In terms of the relative imaginary part of the susceptibility this result can be expressed as

$$\chi_{14}''(\infty)/\chi_{14}''(0) = \Delta n_{14}(\infty)/\Delta n_{14}(0) = -\nu_{23}/\nu_{14}, \quad (2)$$

where ∞ and 0 indicate the limiting cases of infinite and zero saturation powers applied at the frequencies ν_{13} and ν_{24} .

The experiment was performed with the crystal of $K_3(\text{Co,Cr,Fe})(\text{CN})_6$. The ratios of cobalt to the impurities were $\text{Co}:\text{Cr}=200:1$ and $\text{Co}:\text{Fe}=200:1$. The magnetic field of 790 oersteds was directed at $\theta=40^\circ$ in the ac plane of the crystal.⁹ At this orientation $\nu_{23} = \nu_{\text{Fe}} = 1.79$ kMc/sec, $\nu_{14} = 9.63$ kMc/sec and $\nu_{13} = \nu_{24} = 5.71$ kMc/sec. Coincidence of the saturated transitions is convenient experimentally since one can use a doubly resonant cavity.

Figure 2 shows the dependence of $\chi_{14}''(P_{13,24})/\chi_{14}''(0)$

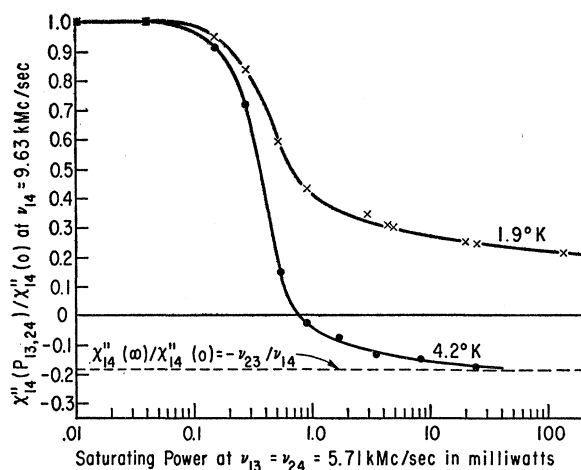


FIG. 2. Relative susceptibility at $\nu_{14}=9.63$ kMc/sec of Cr^{3+} as a function of saturating power applied at $\nu_{13}=\nu_{24}=5.71$ kMc/sec in $K_3(\text{Co, Cr, Fe})(\text{CN})_6$.

⁹ Orientation is specified with respect to orthorhombic axes. See J. M. Baker *et al.*, *Proc. Phys. Soc. (London)* **B69**, 1205, (1956).

on the saturating power applied at the frequency $\nu_{13} = \nu_{24} = 5.71$ kMc/sec. The general theoretical form of this dependence is contained in Eq. (5) of reference 7 and the form is confirmed by the curves of Fig. 2.¹⁰ The points of the lower curve were determined with the crystal at 4.2°K. Inversion takes place for saturating powers larger than 0.80 mw. For very large saturating powers the experimental curve appears to approach the asymptotic value of Eq. (2), $\chi_{14}''(\infty)/\chi_{14}''(0) = -\nu_{23}/\nu_{14} = -0.186$.

The data of the upper curve of Fig. 2 were taken with the same crystal at the temperature of 1.9°K. Inversion was not observed and the experimental $\chi_{14}''(\infty)/\chi_{14}''(0) \simeq +0.2$. Since the cross relaxation is not temperature dependent we conclude that the condition $T_1^{23}(\text{Cr})/T_1(\text{Fe}) \gg 1$ is no longer satisfied. We have

¹⁰ Exact solution of Eq. (5) of reference 7 for other than simple cases presents an intricate theoretical problem. It has been solved only in certain limiting cases for spin system of one ionic species.

measured previously³ this ratio, in a rather preliminary fashion, and found it approximately equal to 85 at 4.2°K and equal to 1 at 1.5°K. The results of the present experiment seem to confirm this very rapid change of $T_1(\text{Fe})$ with temperature.

An experiment was also performed with $\text{K}_3\text{Co}(\text{CN})_6$ containing 0.5% Cr and 3.0% Fe. Inversion of the ν_{14} line was not observed. Bloembergen *et al.*⁷ have discussed the concentration dependence of the cross relaxation in detail. On the basis of their conclusions we interpret our last result as showing the coupling of Fe^{3+} spins not only to the Cr^{3+} spins of ν_{23} transition but also to the spins of other Cr^{3+} transitions.

ACKNOWLEDGMENTS

The author is indebted to several of his colleagues at the Radiation Laboratory and in particular to A. Trammell and G. C. Brown for their patient assistance in the performance of the experiments.

Some Studies of the Superconducting Transition in Purified Tantalum*

J. I. BUDNICK†

International Business Machines Research Laboratory, Poughkeepsie, New York

(Received March 14, 1960; revised manuscript received June 2, 1960)

Extremely sharp magnetic transitions from the superconducting to the normal state are found for highly purified tantalum specimens with residual resistivities approaching $1 \times 10^{-3} \mu$ ohm cm. Negligible flux trapping and pronounced supercooling is found to occur in these samples near the transition temperature T_c .

Values of T_c as high as $4.483^\circ\text{K} \pm .002^\circ\text{K}$ and of the critical field at 0°K, H_0 , as low as 830 ± 8 gauss were found for these specimens. The critical field curve is found to have a maximum deviation from a parabolic temperature dependence of about 3%. For tantalum the transition temperature decreases with increasing residual resistivity in much the same way as that observed by Serin and co-workers in dilute substitutional alloys.

Some investigation is made of the current dependence of the resistance transition in a magnetic field.

INTRODUCTION

TANTALUM metal has in the past presented great problems in purification which limited measurements of the superconducting properties to impure specimens. Numerous authors¹ have investigated various properties of tantalum and in many instances have obtained significantly different results. Quoted values

of H_0 , the critical field at absolute zero vary by several hundred gauss while quoted values of T_c differ by as much as 0.2°K.

In most measurements broad transitions, spurious hysteresis effects, and pronounced flux trapping were observed. These effects are seen to be largely attributable to the presence of small amounts of interstitial impurities, viz., hydrogen, carbon, oxygen, nitrogen, in the tantalum lattice.² Recently several authors³⁻⁵ have shown that purified tantalum yields quite different values of H_0 and T_c .

Preliminary experiments in our laboratory indicated that specimens could be prepared with much lower

* Supported in part by Department of Defense.

† Now at IBM Watson Laboratory, Columbia University, New York, New York.

¹ W. Meissner, Z. Physik **61**, 191 (1930); K. Mendelssohn and J. R. Moore, Phil. Mag. **21**, 532 (1936); J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937); F. B. Silsbee, R. B. Scott, and F. G. Brickwedde, J. Research Natl. Bur. Standards **18**, 295 (1937); J. G. Daunt, A. Horseman, and K. Mendelssohn, Phil. Mag. **27**, 754 (1939); W. H. Keesom and M. Desirant, Physica **8**, 273 (1941); W. T. Zeigler, W. F. Brucksch, Jr., and J. W. Hickman, Phys. Rev. **62**, 354 (1942); H. Preston-Thomas, Phys. Rev. **88**, 325 (1952); R. T. Webber, Phys. Rev. **72**, 1241 (1947); R. D. Worley, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **91**, 1567 (1953); K. Mendelssohn, Nature **148**, 316 (1941).

² A. Wexler and W. Corak, Phys. Rev. **85**, 85 (1952).

³ C. Chou, D. White, and H. L. Johnston, Phys. Rev. **109**, 797 (1958).

⁴ K. Mendelssohn, *Proceedings of the International Conference on Electron Transport in Metals and Solids* [Can. J. Phys. **34**, 1315 (1956)].

⁵ A. B. Calverley (private communication).