Cross Relaxation Effect of Chromium and Iron in $K_3(Co,Cr,Fe)(CN)_6$†

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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 time[1–3] 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} transition[4] 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's[1] 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 $K_3Cr(CN)_6$ 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 Scovil[5] another ion, in our case Fe^{3+}, was added to the cyrstal. The method depends on strong cross relaxation[6,7] between two spin species. When the frequency of the iron line[8] 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 $[T_1(\mathrm{Cr}),T_1(\mathrm{Fe})]$. With equal concentrations of the two paramagnetic ions and if

$$T_1(\mathrm{Cr})/T_1(\mathrm{Fe})\gg1 \qquad (1)$$

the spin temperature of the ν_{23} transition is determined by $T_1(\mathrm{Fe})$ 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 $h\nu_{23}/kT\ll1$. 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

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

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 $K_3(Co,Cr,Fe)(CN)_6$. The ratios of cobalt to the impurities were Co:Cr=200:1 and Co:Fe=200:1. The magnetic field of 790 oersteds was directed at $\theta=40°$ in the ac plane of the crystal.[9] At this orientation $\nu_{23}=\nu_{\mathrm{Fe}}=$ 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 $\chi_{14}''(P_{13,24})/\chi_{14}''(0)$

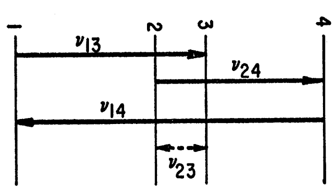

FIG. 1. Schematic diagram of energy levels of an ion with $S=3/2$. To invert populations of ν_{14} line by saturating ν_{13} and ν_{24} lines, condition $T_1^{23}\ll T_1^{ik}$ must be satisfied.

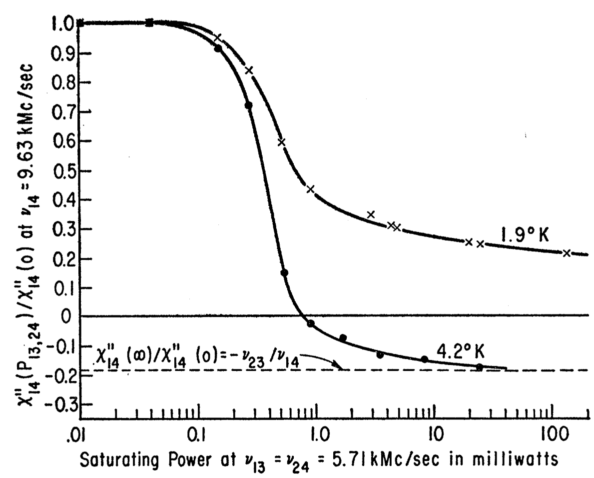

FIG. 2. Relative susceptibility at $\nu_{14}=9.63$ kMc/sec of Cr^{3+} as a function of saturating power applied at $\nu_{13}=\nu_{24}=5.71$ kMc/sec in K_3(Co, Cr, Fe)$(CN)_6$.

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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 $T_1^{23}(\text{Cr})/T_1(\text{Fe})\gg1$ is no longer satisfied. We have measured previously[3] 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(Fe) with temperature.

An experiment was also performed with $K_3Co(CN)_6$ 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.

[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.

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Some Studies of the Superconducting Transition in Purified Tantalum*

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Extremely sharp magnetic transitions from the superconducting to the normal state are found for highly purified tantalum specimens with residual resistivities approaching $1\times10^{-3}\,\mu$ 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°K±.002°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 authors[1] 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 authors[3–5] 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

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