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# Superconductivity and antiferromagnetism in Cr–Mo–Ru alloys

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**Abstract.** $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ alloys with $x = 0$, 3%, 6% or 10% exhibit superconducting properties below 3 K. For low Mo concentrations comparison with theory suggests a coexistence of spin density wave antiferromagnetism and superconductivity while the spin density wave state seems to be absent at higher concentrations. Velocity of sound measurements, however, fail to reveal any spin density wave antiferromagnetic transitions in the alloys. This is attributed to two possibilities: either the nesting portions of the Fermi surface are very small or, as suggested by susceptibility measurements reported recently on $Cr_{75}Ru_{25}$, an unknown magnetic phase appears at low temperatures.

## 1. Introduction

Cr and its alloys are itinerant electron antiferromagnets in which the antiferromagnetic ordering is associated with a spin density wave (SDW) state. The SDW is formed by condensation of electron–hole pairs from electrons on the electron sheet of the Fermi surface and holes on the hole sheet. Gulácsi and Gulácsi (1986) demonstrated that the SDW state can coexist with a superconducting state in Cr alloys, a conclusion previously also reached by Machida (1981). The physical origin of the coexistence of these two states is ascribed to the nesting between the electron and hole Fermi surface sheets in Cr alloys. For small impurity concentrations in Cr the nesting is nearly perfect and SDW formation is strongly favoured which acts destructively on superconducting pairing. Above a certain critical concentration the nesting imperfection increases which weakens the SDW so that superconducting pairing can occur. Only a small region of the Fermi surface sheet nests and leads to the SDW while the remaining portion is used for superconducting pairing.

Cr–Ru alloys with more than 17 at% Ru exhibit superconductivity below $\sim 3$ K (Nishihara *et al* 1986, 1987, Muheim and Müller 1964). Peaks were observed (Nishihara *et al* 1986) in the magnetic susceptibility of these alloys at a temperature of 170 K, nearly independent of concentration in the range $14 \leq c \leq 25$ at% Ru. Nishihara *et al* (1986) suggested that these peaks occur at a Néel temperature of 170 K. This means that superconductivity and antiferromagnetism coexist for $c > 17$ at% Ru and Nishihara *et al* (1987) conclude that their results for $T_c$ follow the theoretical predictions of Gulácsi and Gulácsi (1986).

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Theoretically (Gulácsi and Gulácsi 1986) the superconducting transition temperature $T_c$ of the coexisting state is related to the Néel temperature of the pure SDW phase, i.e. of Cr in the Cr–Ru alloys. If the Néel temperature of the pure phase could be varied and the effect of Ru addition to this varied state on $T_c$ be studied, then the system should be more suited than Cr–Ru for testing the theory. An ideal way to vary the Néel temperature of Cr is to add Mo to it. Mo is isoelectronic with Cr and its addition to Cr does not influence the nature of the SDW but only weakens it through d-band broadening (Cywinski and Hicks 1986). Mo addition decreases $T_N$ linearly down to 0 K at 24 at% Mo (Venter *et al* 1986). The coexisting theory of Gulácsi and Gulácsi (1986) could therefore be tested in a system in which Ru is added to Cr-Mo alloys. In this paper we report on studies of superconductivity in the ternary system $(Cr_{1-x}Mo_x)_{75}Ru_{25}$, where $x$ varies from 0 to 10%. As velocity of sound measurements can usually be very sensitive to probe magnetic transitions in Cr and its alloys (Alberts and Lourens 1984) we searched for such transitions in $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ alloys by measuring the temperature dependence of the velocity of sound.

## 2. Experimental procedure

$(Cr_{1-x}Mo_x)_{75}Ru_{25}$ alloys with $x = 0$, 3%, 6% and 10% were prepared by arc melting in a purified argon atmosphere from 99.99% pure Cr, 99.99% pure Mo and 99.9% pure Ru. Electrical resistance was measured down to 1.25 K, with a temperature resolution of better than 0.01 K, using standard four probe techniques. Velocity of sound measurements were done in the temperature range 4 to 400 K by bonding X-cut 10 Mhz quartz transducers to the samples and using standard ultrasonic methods. All measurements were carried out on as-cast alloys as the previous superconductivity studies on binary Cr–Ru alloys were also done in this state (Nishihara *et al* 1986). X-ray diffraction on the alloys revealed only BCC lines without extra phases. Homogeneity was checked by EDAX analysis at five different points along the length of the resistivity samples which were about 1 cm in length. The Cr, Mo and Ru concentrations were found to be homogeneous to within 3%, 6% and 6%, respectively, of the concentration of each element. The concentrations quoted above are the nominal concentrations. For $x = 0$ the observed value of $T_c = 2.43$ K corresponds very well with the value $T_c = 2.4$ observed by Nishihara *et al* (1986) for $Cr_{75}Ru_{25}$.

## 3. Results

The temperature dependence of the electrical resistance at low temperatures is shown in figure 1. In all samples the resistance sharply drops to zero at temperatures of 2.43 K, 1.89 K, 2.41 K and 2.29 K respectively for $x = 0$, 3%, 6% and 10%. These transition temperatures were taken as the superconductivity transition temperature of each alloy. $T_c$ was defined at the midpoint of the temperature range in which the resistivity falls from 90% to 10% of its value above the transition. The temperature width in which this drop occurs is less than 0.1 K in all cases. This compares well with the transition width of about 0.05 K observed in Cr–Ru alloys by Nishihara *et al* (1986) and of about 0.5 K in Cr–Re alloys by Nishihara *et al* (1985) and by Takeda

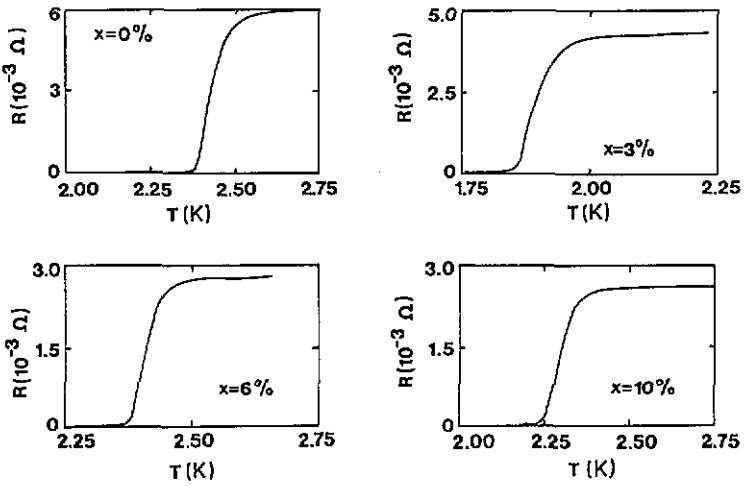


**Figure 1.** Temperature dependence of the electrical resistance ($R$) of $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ alloys at low temperatures. The sharp drop in resistance occurs at the superconducting transition temperature $T_c$.

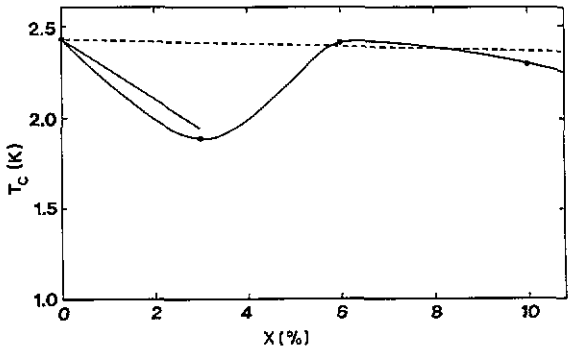


**Figure 2.** The variation of the superconducting transition temperature ($T_c$) with $x$ for $(Cr_{-x}Mo_x)_{75}Ru_{25}$ alloys. The full straight line shows the expected theoretical behaviour when superconductivity and SDW antiferromagnetism coexist while the broken line shows the expected behaviour in the absence of the SDW state. The curve through the experimental points is a guide to the eye.

and Kohara (1984). Figure 2 shows the variation of $T_c$ with $x$. No hysteresis effects at the transition were observed within the experimental limits.

The temperature variation of the velocity of sound for the alloys are shown in figure 3. The experimental errors in the absolute value of the velocity amount to 1% while changes with temperature of 1 in $10^3$ could easily be detected.

## 4. Discussion

The theory of Gulácsi and Gulácsi (1986) was used to calculate the expected change in $T_c$ of the Cr–Mo–Ru alloys on the assumption that superconductivity and SDW antiferromagnetism coexist in these alloys. The critical temperature of the coexisting

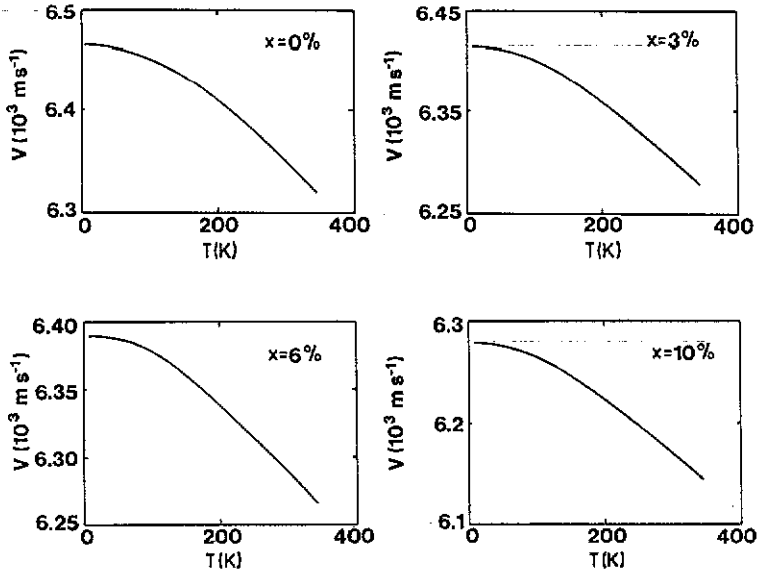


**Figure 3.** Temperature dependence of the velocity of sound of the $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ alloys. The error in the absolute value of the velocity amounts to 1% while changes of the order of 1 in $10^3$ with temperature could easily be detected. Measurements were done at 1 to 2 K intervals. Smooth curves through the experimental points are shown.

phase is given by (Gulácsi and Gulácsi 1986)

$$T_c = c_2(n - n_c)^{1/2} \tag{1}$$

where

$$c_2^2 = \frac{2n_c^4}{\pi^2(\Delta_{S0} - n)^3} \ln(T_{N0}/T_{S0}) \tag{2}$$

and

$$n_c = \Delta_{S0}[2 + \ln(T_{N0}/T_{S0})]. \tag{3}$$

$n$ is proportional to the concentration of the impurity that makes the alloy superconducting. In our case this is the concentration of Ru in $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ which remained constant. $n_c$ is proportional to the critical concentration of Ru, for fixed Mo contents above which superconductivity sets in. $\Delta_{S0}$ is the order parameter for the pure SDW phase with $n = 0$, i.e. for $Cr_{1-x}Mo_x$. $T_{N0}$ is the Néel temperature of the pure SDW phase with $n = 0$, i.e. of $Cr_{1-x}Mo_x$ and $T_{S0}$ is the superconducting transition temperature of the pure BCS superconducting phase, i.e. in the absence of the SDW phase.

When $x$ is varied in $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ the quantities $n_c, c_2, T_{S0}, T_{N0}$ and $\Delta_{S0}$ are also expected to vary. From equations (1), (2) and (3) it follows that the change in $T_c$ of the coexisting phase is given by

$$\frac{dT_c}{dx} = \left(\frac{1}{T_{N0}}\frac{dT_{N0}}{dx} - \frac{1}{T_{S0}}\frac{dT_{S0}}{dx}\right)\left(\frac{2T_c}{n_c}\Delta_{S0} + \frac{T_c}{2\ln(T_{N0}/T_{S0})} - \frac{T_c\Delta_{S0}}{2(n-n_c)}\right)$$
$$+ \frac{1}{\Delta_{S0}}\frac{d\Delta_{S0}}{dx}\left(2T_c - \frac{3}{2}\frac{T_c}{(1-n/\Delta_{S0})} - \frac{1}{2}n_c\frac{T_c}{(n-n_c)}\right). \tag{4}$$

In this equation the quantities $n_c$, $T_c$, $\Delta_{S0}$, $T_{N0}$ and $T_{S0}$ are taken to be the values for $Cr_{75}Ru_{25}$ to determine the initial slope $(dT_c/dx)_{x=0}$.

We proceed in applying equation (4) to the $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ alloys by estimating the quantities on the right-hand side of this equation. $\Delta_{S0}$ was determined from equation (3) by using the critical concentration of Cr–Ru as 16 at% Ru (Nishihara *et al* 1986, 1987), $T_{N0} = 312$ K (that of pure Cr) and $T_{S0} = 5$ K, which although a gross approximation, is reasonable as $T_{S0}$ is larger than the superconducting transition temperature ($T_c = 2.5$ K) of the coexisting phase (Gulácsi and Gulácsi 1986). Using these results, the coefficient of $(1/\Delta_{S0})(d\Delta_{S0}/dx)$ in equation (4) was determined as +3.22 assuming the same proportionality constant between $n$ and the concentration for $n$ and $n_c$. For Cr and its alloys the Néel temperature may be taken to be proportional to the antiferromagnetic SDW energy gap (Koehler *et al* 1966), which is proportional to the ordering parameter $\Delta_{S0}$. We therefore assume

$$\frac{1}{\Delta_{S0}}\frac{d\Delta_{S0}}{dx} \simeq \frac{1}{T_{N0}}\frac{dT_{N0}}{dx}$$

which gives

$$\frac{1}{\Delta_{S0}}\frac{d\Delta_{S0}}{dx} = -0.045/\text{at\% Mo}$$

for $Cr_{1-x}Mo_x$ alloys (Venter *et al* 1986). This gives a contribution of −0.145 K/at% Mo from the last term in equation (4) to $dT_c/dx$.

To estimate the contribution from the first term in equation (4) we note that $(1/T_{S0})(dT_{S0}/dx)$ is expected to be much smaller than $(1/T_{N0})(dT_{N0}/dx)$ ($\sim -0.045$/at% Mo), the reason being that the change in $T_{S0}$ with Mo concentration is expected to result mainly from a mass difference when the heavier Mo atoms, which are isoelectronic with Cr atoms and which have very similar band structures, replace the lighter Cr atoms. One therefore expects the effect on $T_{S0}$ to be very similar to the well known isotope effect in superconductors which is known to give a transition temperature proportional to the negative square root of the mean isotopic mass. Using this approximation one gets

$$\frac{1}{T_{S0}}\frac{dT_{S0}}{dx} \sim -0.002/\text{at\%Mo}.$$

With this value and assuming the values of $n_c, T_{N0}, T_{S0}$ and $\Delta_{S0}$ as before, the first term in equation (4) was found to contribute a value of −0.033 K/at% Mo to $dT_c/dx$. Thus from equation (4) one estimates $(dT_c/dx)_{x=0} = -0.18$ K/at% Mo for $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ alloys if the antiferromagnetic and superconducting phases coexist. By using a Taylor series expansion of $(1/T_c)(dT_c/dx)$, the change in $dT_c/dx$ in going from $x = 0$ to $x = 3\%$ was found to be only 2%. $T_c$ therefore decreases theoretically nearly linearly up to at least $x = 3\%$.

If, on the other hand, the superconducting phase and the SDW state do not coexist one would expect only the above-mentioned 'isotope effect' to give rise to a decrease in $T_c$ when Cr atoms are replaced by Mo atoms. This effect is estimated as above to result in $dT_c/dx \simeq -0.006$ K/at% Mo.

In figure 2 the two theoretical limits, namely $T_c$ as calculated from equation (4) and as calculated by assuming only the 'isotope effect' to be applicable, are also shown. The

initial decrease of the experimental curve corresponds well with the coexisting situation (equation (4)) while the portion at larger $x$ corresponds better with the 'isotope effect' calculation. It thus appears as though the SDW state and superconductivity coexist at the lower Mo concentrations but that antiferromagnetism is absent for larger $x$.

We used velocity of sound measurements to probe the existence of antiferromagnetism in the $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ alloys. Large anomalies can be observed in the velocity of sound of Cr and its alloys at the SDW antiferromagnetic transition temperature $T_N$ (Alberts and Lourens 1984). As shown in figure 3, the results failed to reveal any SDW antiferromagnetic transition. A similar situation was also found in Cr–Ru and Cr–Re alloys (Alberts 1988, 1989) where the peaks in the magnetic susceptibility observed by Nishihara *et al* (1986) do not show in elastic constant measurements.

In this regard it may be mentioned that Nishihara *et al* (1987) observed a two step-like decrease in the electrical resistance of $Cr_{75}Ru_{25}$ with decreasing temperature. A sharp change in slope occurs at about 170 K where the susceptibility peak occurs. They attribute this behaviour to magnetic scattering below 170 K. This is however not the normal behaviour expected for SDW itinerant electron antiferromagnetism for which a hump-like behaviour in the resistivity is usually observed at $T_N$.

The temperature dependence of the electrical resistance of the $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ samples in the temperature range 4 K to 300 K is shown in figure 4. A two-step-like behaviour, similar to that observed by Nishihara *et al* (1987) for $Cr_{75}Ru_{25}$, is also observed for $x = 0$, 3% and 6% but at temperatures different from 170 K. For $x = 10\%$ the step-like behaviour is absent. A step-like behaviour in the resistance is, however, not necessarily indicative of a SDW antiferromagnetic transition. This is illustrated by the behaviour of two Cr–Mo–Si alloys (Smit and Alberts 1989, 1990) shown in figure 5. These two alloys are known from several experimental observations (Smit and Alberts 1989, 1990) to remain paramagnetic down to 0 K. They display a behaviour very similar to that observed for the Cr–Mo–Ru alloys; the behaviour of $(Cr_{0.97}Mo_{0.03})_{95}Si_5$ (figure 5(a)) is very similar to that of $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ for $x = 0$, 3% and 6% while that of $(Cr_{0.88}Mo_{0.12})_{98.6}Si_{1.4}$ (figure 5(b)) is again similar to the behaviour of the Cr–Mo–Ru sample with $x = 10\%$. We conclude that the susceptibility observations of Nishihara *et al* (1986, 1987) at 170 K is not necessarily indicative of a SDW antiferromagnetic transition, but may point to an unknown magnetic transition which may also occur in Cr–Mo–Ru alloys with the lower Mo concentrations. The possibility (Nishihara *et al* 1987), however, exists that only a very small portion of the Fermi surface may contribute to SDW formation in these alloys, thereby suppressing the resistivity hump and the anomaly in the velocity of sound at $T_N$. Neutron diffraction experiments are required to settle this point. It is interesting in this regard that the behaviour of $T_c$ of $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ at low $x$ seems to follow the predictions of the coexisting theory of Gulácsi and Gulácsi (1986) in which the magnetic phase that coexists with the superconducting phase is a SDW antiferromagnetic one.

## 5. Conclusion

$(Cr_{1-x}Mo_x)_{75}Ru_{25}$ alloys with $x = 0$, 3%, 6% and 10% are superconducting below 2.6 K and provide an ideal system to test theories of coexistence of superconductivity and antiferromagnetism. For low Mo concentrations the alloys behave, by comparison with theoretical predictions, as though superconductivity and SDW antiferromagnetism coexist, while the behaviour for higher Mo concentrations is more in line with a situation where the SDW phase is absent. Velocity of sound measurements however fail

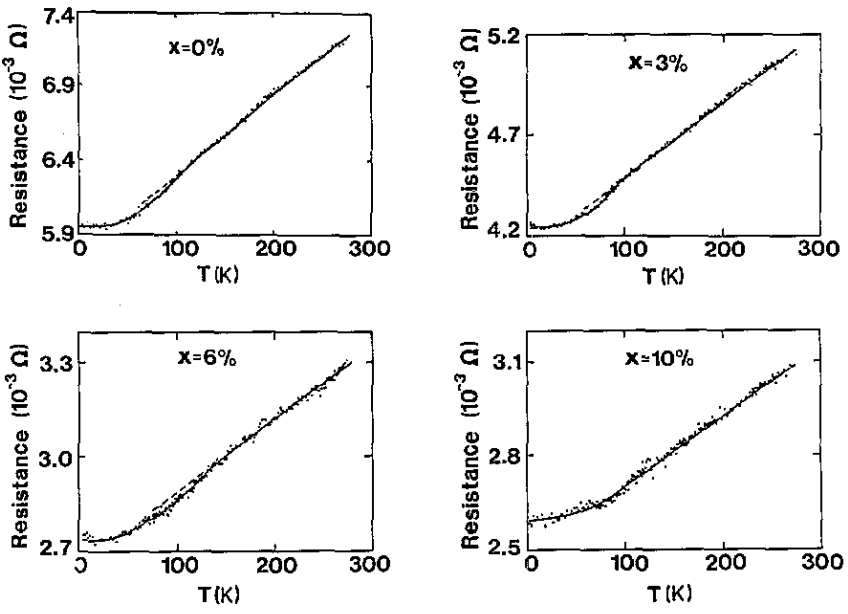


**Figure 4.** Temperature dependence of the alloys $(Cr_{1-x}Mo_x)_{75}Ru_{25}$ electrical resistance in the temperature range 4 to 300 K.

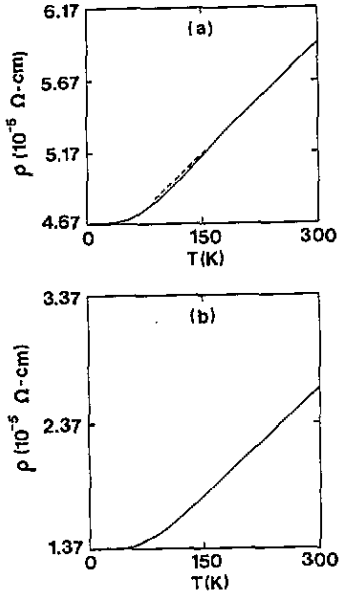


**Figure 5.** Temperature dependence of the electrical resistivity ($\rho$) of (a) $(Cr_{0.97}Mo_{0.03})_{95}Si_5$ and (b) $(Cr_{0.88}Mo_{0.12})_{98.6}Si_{1.4}$. Data sampling took place at 0.5 K intervals and the curves shown are smooth curves through the results. The error in the absolute values of the resistivity is about 1% while change of 1 in $10^4$ with temperature could easily be detected.

to reveal any SDW antiferromagnetic transitions in the alloys. This may be due to the nesting portions of the Fermi surface being too small to show effects in the velocity of sound or, as suggested by susceptibility measurements of Nishihara *et al* (1986, 1987) on Cr–Ru, to another presently unknown, magnetic phase that appears at low temperatures.

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