Calorimetric studies of the order of magnetic phase transitions in Cr and some Cr alloys at the Néel point

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Abstract. In order to determine the order of the magnetic transition of pure Cr and some Cr alloys at the Néel point, we have performed direct measurements of the latent heat. In good agreement with the recent proposal of Young and Sokoloff, our results reveal that the transition between the paramagnetic and the incommensurate spin density wave structure is of the first order while the transition becomes of the second order when it is between the paramagnetic and the commensurate spin density wave structure.

1. Introduction

It is a well established fact that chromium undergoes a cooperative phase transition from a paramagnetic (P) to an antiferromagnetic state at the Néel temperature T_N. In the antiferromagnetic state, chromium possesses a sinusoidal spin density wave structure, transversely polarized between T_N and the spin-flip temperature T_{SF} and longitudinally polarized below T_{SF}. According to neutron diffraction studies by Arrott et al (1965), T_N is about 312 K and T_{SF} about 115 K. The spin density wave (SDW) is incommensurate with the reciprocal lattice and is characterized by a wavevector q in the first Brillouin zone, directed along one of the cube axes with the components $(1 - \delta, 0, 0)$, the quantity δ being temperature dependent and equal to 0·037 at T_N. On increasing the electron to atom ratio by alloying chromium with elements on the right hand side of chromium in the periodic table, the incommensurate sinusoidal spin density wave (ISSDW) structure is eventually destroyed giving rise to a commensurate sinusoidal spin density wave (CSSDW) structure, viz $\delta = 0$. In general the Néel temperature decreases with increasing solute content in the ISSDW state and increases in the CSSDW state. According to Arrott et al (1965), the P–ISSDW transition in pure chromium is of first order. There have been some demonstrations of first order transitions in chromium rich alloys at T_N as well, all of which seem to be between the P and the ISSDW state.

There are only a few theoretical calculations of the latent heat associated with the anomalous first order transition at T_N for chromium, most theories predicting a second order transition. Kimball and Falicov (1968) and Kimball (1969) proposed a model which gave a first order transition. The model used was a two-band model such that one band resembled the free electrons and the other a tight binding d band.

The magnetic periodicity, incommensurate with the lattice, varies slightly with interaction strength. The calculations were performed within the Hartree–Fock approximation. The latent heat obtained was 0.05 J mole^{-1} while experimental values of the order 1 J mole^{-1} have been estimated from specific heat measurements (Garnier and Salamon 1971, Weber and Street 1972, Polovov 1974).

The effective spin–lattice coupling, resulting from the lattice dependence of the nesting area of the electron and hole surface, was ignored in the model of Kimball and Falicov. On the other hand, the large concentration dependence of the transition temperature indicates a strong spin–lattice coupling which might be responsible for the discrepancy between the observed and calculated values. Shimizu (1970) has calculated the latent heat with a model where the increase in free energy density, due to a given distribution of the antiferromagnetic magnetization, is written as a function of temperature, magnetic field, the spatial distribution of the magnetic moment and its derivatives. The latent heat calculated from this model is 5.4 J mole^{-1}.

Nakanishi and Maki (1972) have studied a two-band model where the Fermi surfaces of the electron band and the hole band are spherical but different in size. They find the ISSDW to result in the lowest free energy. They also find at least in the vicinity of the triple point, dividing the regions of the incommensurate and the commensurate spin density wave structures, a first order transition at the Néel point. The latent heat calculated from their model is 3.1 J mole^{-1}.

Young and Sokoloff (1974) have recently proposed a model where the mechanism for the occurrence of a first order transition is based on the existence of harmonics in the spin wave. They performed a calculation based on a simple three-band model with one electron band and two hole bands and showed that there exists a range of values of parameters relevant for chromium for which the gap equation gives a discontinuous drop of the gap in the electron energy spectrum to zero at a finite temperature, characteristic of a first order transition. The gap is caused by the periodicity of the SDW. The absence of harmonics on the other hand leads to a second order transition. As there are harmonics in the ISSDW but not in the CSSDW structure, this implies that the P–ISSDW transition should be of the first order and the P–CSSDW transition of the second order. Young and Sokoloff also pointed out that the model of Nakanishi and Maki (1972) does include harmonics of the spin wave although not explicitly stated in the paper of Nakanishi and Maki. The reason for the first order transition in their model might therefore be the one proposed by Young and Sokoloff.

The aim of the present investigation was to study the transition at T_N in some chromium alloys by direct measurements of the latent heat and to correlate the appearance of a first order transition with the magnetic structure of the material. For comparison, measurements have also been performed on pure chromium, where the first order transition is a well established fact. Our results are in qualitative agreement with the predictions of Young and Sokoloff (1974).

2. Experimental details

2.1. Equipment and measuring technique

The change of heat content due to the change of spin order was measured by a sensitive differential calorimeter. The details of the equipment have been described elsewhere (Benediktsson 1974). The measurements were performed by changing the

temperature of the measuring cell linearly with time. The temperature change is usually of the order of 1 mdeg s^{-1}. The temperature of the sample is followed by a sensitive potentiometer. The signal from the differential thermocouple is biased by a nanovolt bridge, preamplified by a photocell galvanometer and finally registered on a two-channel recorder as the rate of change of energy against time, together with the temperature of the measuring cell.
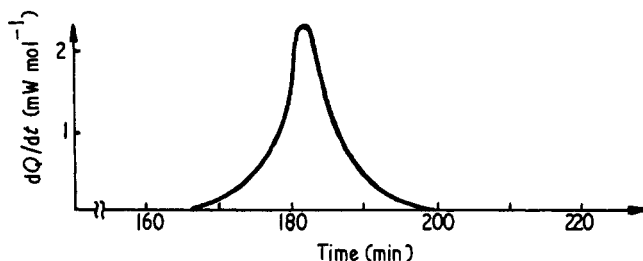

Figure 1. The rate of change of energy against time for Cr–SC.

The calibration of the sensitivity of the cell is performed using the Peltier effect. The sensitivity is of the order of 0·3 μW per mm deflection on the recorder. The temperature range of the apparatus is at present approximately 295–600 K.

In order to test the measuring technique, we have made repeated runs on pure chromium samples. The reproducibility in the latent heat determinations was better than ± 0.02 J $mole^{-1}$. This is well within the absolute accuracy of the present technique, which is estimated to be about ± 0.08 J $mole^{-1}$ for pure chromium.

The rate of change of energy dQ/dt against time for a pure chromium single crystal (SC) sample is shown in figure 1. A marked peak in dQ/dt is obtained within a narrow range of temperatures, some tenths of a degree, around T_N which is assumed to be the temperature corresponding to the maximum of the peak. The energy evolved or absorbed when passing T_N from a region just above or just below the transition point is the latent heat of the process, which is obtained by integrating the area under the curve in figure 1.

The curve shows dQ/dt reduced for the background which varies linearly due to a slight difference in the thermal capacity of the dummy and the sample. The slope of the background is slightly changed at T_N due to the change in specific heat. The uncertainty in the background near T_N is still rather small and it is included in the uncertainty of the calculated value of the latent heat.

A first order transition, being characterized by a certain latent heat, will correspond to a well defined peak in the rate of change of energy curve within a small region around the transition point. Therefore the results of figure 1 clearly show, for chromium, the first order character of the transition. If the transition had been of higher order, no change of dQ/dt would have been observed at the critical temperature which will be the case for some of the chromium alloy samples discussed below.

2.2. Samples measured

Seven samples of chromium rich alloys have been measured, *viz* Cr–0·3 at% W, Cr–0·6 at% Mo, Cr–0·4 at% Co, Cr–2·2 at% Co, Cr–2·7 at% Co, Cr–0·3 at% Al

and Cr–1·9 at% Al. The Néel temperature of these alloys have been determined previously from electrical resistivity measurements by Arajs *et al* (1973), where details about the preparation of the samples can be obtained. For comparison two samples of pure chromium were also measured. One of the samples was a single crystal, the sample being cut from the crystal used in the resistivity and thermal expansion measurements of Stebler (1970) and Stebler *et al* (1970). Its purity is 99·996%. The other chromium sample was a polycrystalline one of the purity of 99·999%, from the original stock of chromium used by Arajs *et al* (1973).

All samples except the single crystal of pure chromium, were annealed *in vacuo* at 1300 K for 50–90 h and then furnace-cooled to room temperature before the measurements in the calorimeter. The weight of the Cr and Cr alloy specimens was between 0·2 and 1·2 g.

3. Results and discussion

The measurements on annealed single crystalline and polycrystalline chromium show a small but well defined change of energy at T_N. The latent heats and the values of T_N are given in table 1. The results are in good agreement with previous measurements of specific heat on chromium (Garnier and Salamon 1971, Weber and Street 1972, Polovov 1974) with the exception of the results of Sze and Meaden (1971), which are about 100% higher than our results. The reason for this discrepancy is not known.

For all chromium samples it was observed that, when measuring with increasing temperature, the latent heat was slightly higher than when measuring with decreasing temperature. It is possible that the reason for this is the same as the one responsible for the relaxation effect observed by Stebler *et al* (1970) and by Weber and Street (1972). The average value of the heat detected when passing T_N from above or below has been taken as the actual value of the latent heat. There is no significant difference in latent heat or T_N between the annealed single crystal of pure chromium and the polycrystalline samples. The peak of the dQ/dt curve is only somewhat sharper in the former case.

For chromium alloys, our measurements reveal a first order transition in Cr–0·3 at% W, Cr–0·6 at% Mo, Cr–0·4 at% Co and Cr–0·3 at% Al and a second order

Table 1. Latent heats and values of T_N.

	T_N (K)		Latent heat (J mole^{-1})	
	Present work	Literature	Increasing temp	Decreasing temp
Cr–sc	311·4	311·5[a]	1·10 ± 0·10	0·97 ± 0·10
Cr–pc	312	312[b]	1·06 ± 0·10	0·97 ± 0·10
Cr–0·6 at% Mo	303	304[b]	0·80 ± 0·08	0·80 ± 0·08
Cr–0·3 at% W	303	304[b]	0·98 ± 0·10	0·85 ± 0·09
Cr–0·4 at% Co	298	298[b]	0·44 ± 0·10	—
Cr–2·2 at% Co	300	300[b]	0	0
Cr–2·7 at% Co	325	324[b]	0	0
Cr–0·3 at% Al	300	300[b]	0·36 ± 0·06	0·35 ± 0·06
Cr–1·9 at% Al	310	310[b]	0	0

[a]Stebler 1970; [b]Arajs *et al* 1973.

transition in Cr–2·2 at% Co, Cr–2·7 at% Co and Cr–1·9 at% Al. So far there have been no measurements or estimates of the latent heat in chromium rich alloys reported except for those of Åström *et al* (1973). Nevertheless, as we will discuss shortly, there are some other experimental manifestations of first order transitions in these chromium rich alloys at the Néel temperature.
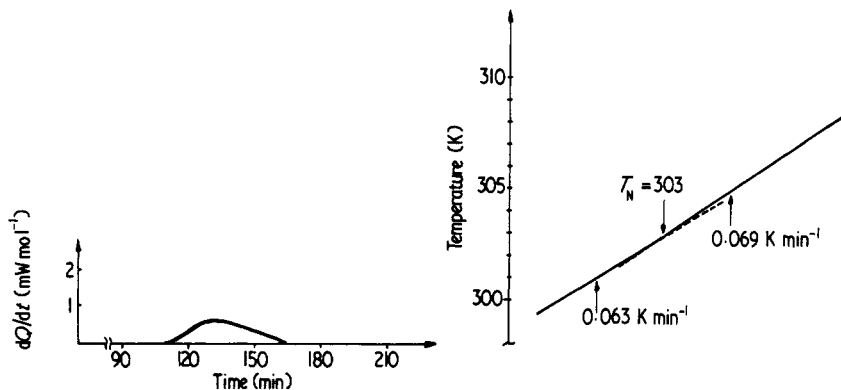

**Figure 2.** The rate of change of energy against time for Cr–0·3 at% W.

When chromium is alloyed with the isoelectronic metals W or Mo, the Néel temperature has been found to decrease by 14 K and 28 K per at% respectively (Arajs *et al* 1973). In figure 2, dQ/dt for the Cr–0·3 at% W sample is given against time. In the same diagram the corresponding temperature of the sample is plotted against time. At the Néel temperature there is a small break in the linear temperature against time curve due to the difference in the specific heat between the paramagnetic and the antiferromagnetic phases. This break can be used to determine the Néel point. Neutron diffraction studies of the Cr–W system by Koehler *et al* (1966) show that the antiferromagnetic state is an ISSDW state. Their data have been interpreted as revealing a second order transition at T_N but a least square fit to their data, which gives a better fit to the measured points than the Brillouin function of spin $\frac{1}{2}$ used by Koehler *et al*, indicates the possibility of a first order transition for the alloys of 1·47, 1·89, 3·64 and 3·65 at% W. The data of Koehler *et al* for these concentrations are shown in figure 3 with our extrapolations (broken lines) for the 1·47 and the 3·64 at% alloys. The latent heat of Cr–0·3 at% W at T_N reported in the present investigation, $L = 0·9$ J mole^{-1}, is slightly lower than in pure chromium in qualitative agreement with the decrease of jump in the square root of the integrated intensity of the magnetic satellite at T_N shown in figure 3. Neutron diffraction studies of the Cr–Mo system by Koehler *et al* (1966) reveal an ISSDW state as in the Cr–W system.

The Cr–Co system is more complicated than the Cr–W and Cr–Mo systems. Studies of the variation of the Néel temperature against Co concentration (Arajs *et al* 1973) show that T_N decreases slightly up to 1·5 at% Co, then increases between 1·5 and 2·9 at% but decreases again with a further increase in the Co concentration. The neutron diffraction studies of the Cr–Co system by Endoh *et al* (1968) and Werner *et al* (1967) indicate that the ISSDW state for concentrations below approximately 1·5 at% Co, coinciding with the minimum in T_N. According to Endoh *et al* (1968), the magnetic moment remains constant while the wavevector of the SDW

increases with increasing Co concentration in the ISSDW state, thus approaching the CSSDW state.

There are rather few reports of investigations on the Cr–Al system. Studies of the variation of the Néel temperature against concentration (Arajs *et al* 1973) reveal a minimum in T_N at 1·1 at% Al. Neutron diffraction studies of the Cr–Al system by Kallel and De Bergevin (1967) reveal that the ISSDW is stable for concentrations below 1·1 at% Al and that the CSSDW is stable above that concentration.

There have been some reports of first order phase transitions also in other chromium rich alloy systems. The first order phase transitions in the Cr–Mn (Bastow 1966) and the Cr–Re (Lebech and Mikke 1972) systems are clearly correlated to the P–ISSDW transition whereas the transition becomes of second order for the P–CSSDW transition.
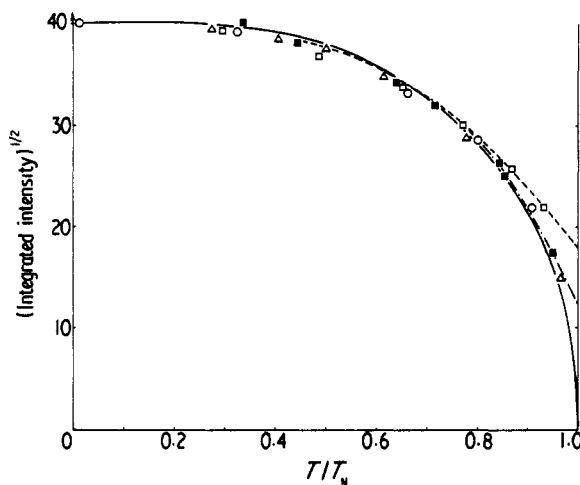
Figure 3. The neutron diffraction data of Koehler *et al* (1966) for some Cr–W alloys: □ Cr–1·47 at% W, △ Cr–1·89 at% W, ■ Cr–3·64 at% W, ○ Cr–3·65 at% W. The full curve is the $B_{1\,2}$ (x) function fitted to the data; the broken curve is the least square fit to the data for Cr–1·47 at% W; the chain curve is the least square fit to the data for Cr–3·64 at% W.

Arrott *et al* (1967) report a first order transition between P and the CSSDW state for Cr–2·3 at% Fe. This seems however to be in conflict with the satellite reflections which they observed at T_N. The observations can however be explained if there are two first order transitions within a narrow temperature range, *viz* a P–ISSDW transition at 250 K and an ISSDW–CSSDW transition at 235 K. This suggestion is in agreement with the phase diagram given by Arajs (1970). The transition between ISSDW and CSSDW is of the first order according to Kotani (1974). This has been demonstrated for Cr–Mn by Kazama and Watanabe (1973).

Our calorimetric measurements on pure chromium and chromium alloys at the Néel temperature, as well as the above related measurements, therefore support the theory of Young and Sokoloff, *viz* that the P–ISSDW transition is a first order phase transition while the P–CSSDW transition is a second order phase transition. On the other hand the latent heat calculated for chromium from the model of Young and Sokoloff seems to be somewhat too large compared with the experimental results.

In this respect, the model of Nakanishi and Maki (1972) is in better agreement with the experimental results.

Acknowledgments

References

Arajs S 1970 *J. Less-Common Metals* **22** 519–22
Arajs S, Rao K V, Åström H U and De Young T F 1973 *Physica Scripta* **8** 109–112
Arrott A, Werner S A and Kendrick H 1965 *Phys. Rev. Lett.* **14** 1022–4
—— 1967 *Phys. Rev.* **153** 624–31
Åström H U, Benediktsson G and Rao K V 1973 *Proc. 2nd Nordik Symp. on Thermal Analysis, Risö* (Stockholm: Nordforsk) pp 62–67
Bastow T I 1966 *Proc. Phys. Soc.* **88** 935–42
Benediktsson G 1974 *Tech. Rep.* TRITA-FYS-5011, Stockholm
Endoh Y, Ishikawa Y and Ohno H 1968 *J. Phys. Soc. Japan* **24** 263–70
Garnier P R and Salamon M B 1971 *Phys. Rev. Lett.* **27** 1523–6
Kallel A and De Bergevin F 1967 *Solid St. Commun.* **5** 955–8
Kazama N and Watanabe H 1973 *J. Phys. Soc. Japan* **31** 943
Kimball J C 1969 *Phys. Rev.* **183** 533–45
Kimball J C and Falicov L M 1968 *Phys. Rev. Lett.* **20** 1164–6
Koehler W C, Moon R M, Trego A L and Mackintosh A R 1966 *Phys. Rev.* **151** 405–13
Kotani A 1974 *J. Phys. Soc. Japan* **36** 103–11
Lebech B and Mikke K 1972 *J. Phys. Chem. Solids* **33** 1651–63
Nakanishi K and Maki K 1972 *Progr. Theor. Phys.* **48** 1059–79
Polovov T M 1974 *Zh. Eksp. Teor. Fiz.* **66** 2164–77 (in Russian)
Shimizu M 1970 *Progr. Theor. Phys.* Suppl. **46** 310–24
Stebler B 1970 *Physica Scripta* **2** 53–6
Stebler B, Andersson C G and Kristensson O 1970 *Physica Scripta* **1** 281–5
Sze N H and Meaden G T 1971 *Phys. Lett.* **35A** 329–30
Weber R and Street R 1972 *J. Phys. F: Metal Phys.* **2** 873–7
Werner S A, Arrott A and Kendrick H 1967 *J Appl. Phys.* **38** 1243–4
Young C Y and Sokoloff J B 1974 *J. Phys. F: Metal Phys.* **4** 1304–19