

dielectric constant on the two sides of the transition temperature. This effect is not present in the lower temperature transition, where the difference in the dielectric constants are less pronounced. Preliminary measurements on a Rochelle salt crystal indicate a white noise spectrum, but the noise level is too small to be measured accurately. The lower noise in Rochelle salt compared to barium titanate is consistent with the difference in the saturation polarization of the two materials.

These results suggest that the noise may be due to a thermal Barkhausen effect produced by the creation or destruction of polarized domains as the crystal passes through the transition temperature. At very slow temperature drift rates the interval between individual noise pulses becomes so long that the integrated noise level is small. If this interpretation is correct the data suggest that similar domain configurations are active at both the 120°C transition and the 0°C transition in barium titanate, since the noise levels are the same. The  $1/f$  characteristic of the spectrum may imply an exponential distribution of domain sizes according to the conventional interpretation of  $1/f$  noise.<sup>5</sup>

<sup>5</sup> A. van der Ziel, *Fluctuation Phenomena in Semiconductors* (Academic Press Inc., New York, 1959), p. 56.

## V. CONCLUSIONS

These experimental results appear to establish the existence of critical-point polarization fluctuations in ferroelectric crystals at the Curie temperature. The polarization fluctuations can be interpreted in terms of Nyquist noise associated with the crystal conductance and therefore noise measurements can be used to determine the true crystal impedance at and near the transition temperature. The fact that the polarization noise density in triglycene sulfate is a simple relaxation spectrum indicates that the loss mechanisms at the Curie temperature in this material can be characterized by a single relaxation time. It appears that this time constant is relatively independent of temperature near the transition temperature. Ferroelectric crystals having a first-order transition exhibit a thermal Barkhausen effect which may prove useful in examining the inherent domain size distribution in such crystals.

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## Superconductivity of Chromium Alloys

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The superconducting properties of Cr-Ru, Cr-Rh, and Cr-Ir alloys have been investigated and the transition temperatures have been determined as a function of composition and of valence-electron concentration.

The Cr-Ru system contains three superconducting phases all of which have a homogeneity range. A hexagonal close-packed alloy containing 50 at. % Cr has a transition temperature of 1.65°K. The sigma-phase type compound Cr<sub>2</sub>Ru has a transition temperature of 2.0°K and Cr<sub>3</sub>Ru which crystallizes in the  $\beta$ -W type structure becomes superconducting at 3.3°K.

The hexagonal close-packed alloys in the Cr-Rh system are superconducting. The transition temperature of an alloy containing 70 at. % Cr is 1.1°K. Weak ferromagnetism was observed in cold-worked hexagonal close-packed alloys containing approximately 60 at. % Cr.

There are two superconducting phases in the Cr-Ir system. A hexagonal close-packed alloy containing 72 at. % Cr has a transition temperature of 0.83°K. An alloy with the  $\beta$ -W type structure containing 85 at. % Cr becomes superconducting at 0.77°K.

Both superconductivity and ferromagnetism occur in the Cr-Ir system. The critical conditions for the occurrence of both phenomena are discussed.

## INTRODUCTION

THE only reported superconductors containing chromium are the solid solutions of chromium in hexagonal and in cubic titanium.<sup>1</sup> Chromium and molybdenum are in the same column of the periodic table and form many isomorphous compounds and inter-

mediate phases with the noble metals of the VIIIth column. Recently, molybdenum has been reported as a superconductor<sup>2</sup> and many of the molybdenum alloys are known superconductors.<sup>3</sup> For the latter reason, a study of the superconducting properties of Cr alloys was undertaken.

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<sup>1</sup> B. T. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, *Phys. Rev.* **115**, 1597 (1959).

<sup>2</sup> T. H. Geballe, B. T. Matthias, E. Corenzwit, and G. W. Hull, Jr., *Phys. Rev. Letters* **8**, 313 (1962).

<sup>3</sup> B. T. Matthias, *Phys. Rev.* **97**, 74 (1955).

The superconducting properties of Cr-Ru, Cr-Rh, and Cr-Ir alloys have been investigated. Two essential factors for the study are the availability of high-purity Cr and the equipment for measuring transition temperatures down to 0.3°K. The Cr purity is very important since many elements will react with Cr to form ferromagnetic phases. The Cr used in the present study was obtained from the United Mineral Company and was 99.999% Cr. Ru, Rh, and Ir sponge were obtained from Engelhard Industries. An analysis of the metals was not available. The alloys were prepared by reacting the appropriate amounts of the elements in a small argon atmosphere arc furnace. The superconducting transition temperatures were determined in a helium-3 cryostat using the sensitive ac method of Schawlow and Devlin.<sup>4</sup> The structure of the phases was determined by the x-ray powder diffraction method.

#### CHROMIUM-RUTHENIUM SYSTEM

The Cr-Ru system has been investigated by Raub and Mahler<sup>5</sup> and by Greenfield and Beck.<sup>6</sup> Recently, Savitskii, Terekhova, and Birun<sup>7</sup> determined the equilibrium diagram of the system. The solid solubility of Cr in hexagonal close-packed Ru extends to more than 50 at. % Cr. A tetragonal sigma phase exists in the region of 66 at. % Cr and a cubic  $\beta$ -W type phase in the region of 75 at. % Cr. Both phases have a homogeneity range. In addition, Raub and Mahler<sup>5</sup> report a Cr<sub>4</sub>Ru phase of unknown structure. The x-ray diffraction results of the present study agree with the previously reported data for the alloys in the system, with the exception of the Cr<sub>4</sub>Ru phase. Diffraction evidence for this phase was not found in alloys of this composition which had been annealed at 800–850°C. The powder patterns for these alloys contain the lines of the  $\beta$ -W type phase and of the body-centered Cr solid solution.

The transition temperatures are plotted as a function of composition and of valence electrons/atom in Fig. 1. When Cr is dissolved in hexagonal Ru, the transition temperature decreases from about 0.5°K for pure Ru to less than 0.3°K for a 20 at. % Cr alloy. For the hexagonal close-packed alloys containing more than 30 at. % Cr, the transition temperature again rises and increases to 1.65°K for a 50 at. % Cr alloy.

Both the sigma phase and the  $\beta$ -W phase are superconducting. A sigma-phase alloy, Cr<sub>2</sub>Ru, has a transition temperature of 2.0°K and an annealed  $\beta$ -W compound, Cr<sub>3</sub>Ru, has a transition temperature of 3.3°K. An unannealed alloy containing 87.5 at. % Cr is superconducting at 1.2°K. The predominant phase in this alloy has the  $\beta$ -W type structure. The solid solution of Ru in body-centered Cr is not superconducting above 0.3°K.

Correlation of the phases present in the x-ray diffrac-

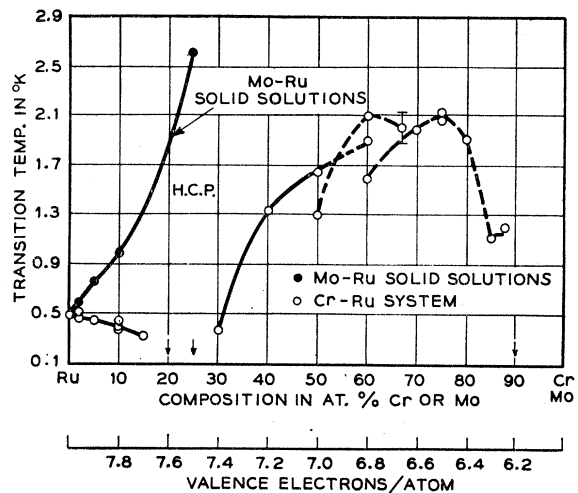


FIG. 1. Superconductivity in the Cr-Ru system and in Mo-Ru solid solutions.

tion patterns with the transition into the superconducting state is less certain in alloys containing 50 at. % or more Cr. The alloys in the 50 to 60 at. % Cr region have more than one transition temperature indicating the presence of more than one superconducting phase. In addition, it was difficult to obtain representative powder samples for the x-ray analysis of alloys containing more than 70 at. % Cr because of the extreme hardness of these alloys. For these reasons the curves in Fig. 1 for alloys of more than 50 at. % Cr are drawn with dashed lines.

The superconducting behavior of the alloys in the Ru-rich region of the system is very interesting because of the information it gives about superconductivity in dilute Cr solid solutions. From the variation in valence electrons/atom, one would have expected a steep monotonic rise in the transition temperature similar to the corresponding Mo-Ru solid solutions. The initial lowering of the transition temperature by the addition of Cr, followed by a subsequent rise in the transition temperature with increasing amounts of Cr, may be due to a ferromagnetic interaction between Cr atoms when in sufficient dilution. At higher concentrations of Cr this interaction is no longer important. Magnetic susceptibility measurements lend qualitative support to this description.

#### CHROMIUM-RHODIUM SYSTEM

Raub and Mahler<sup>5</sup> and Greenfield and Beck<sup>6</sup> have determined the phases present in this system. In addition to the body-centered and face-centered terminal solid solutions, a hexagonal close-packed phase and a  $\beta$ -W type phase are present in the system. The two cubic elements form a hexagonal close-packed alloy with a homogeneity range from about 25 to about 80 at. % Cr. The superconducting transition temperatures of this phase are plotted as a function of composition and of

<sup>4</sup> A. L. Schawlow and G. E. Devlin, Phys. Rev. **113**, 120 (1959).

<sup>5</sup> E. Raub and W. Mahler, Z. Metallk. **46**, 210 (1955).

<sup>6</sup> P. Greenfield and P. A. Beck, J. Metals **8**, 265 (1956).

<sup>7</sup> E. M. Savitskii, V. F. Terekhova, and N. A. Birun, Zhur. neorg. Khim. **6**, 1960 (1961).

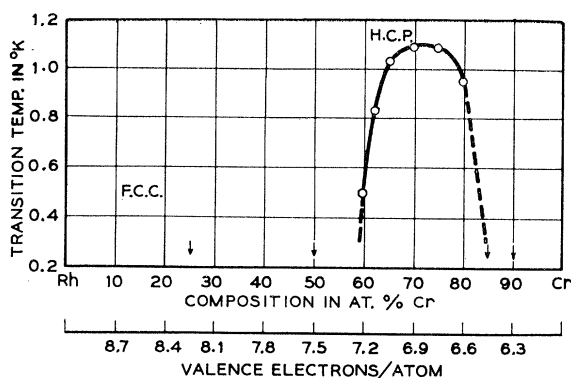


FIG. 2. Superconductivity in the Cr-Rh system.

valence electron concentration in Fig. 2. A maximum in the transition temperature occurs at 6.9–6.75 valence electrons/atom. The  $\text{Cr}_3\text{Rh}$ ,  $\beta$ - $W$  type, phase is not superconducting above 0.3°K.

Raub<sup>8</sup> reported that the hexagonal close-packed Cr-Rh alloys show ferromagnetic properties. We were unable to detect any ferromagnetism in the as-cast alloys. If, however, the melts containing about 60 at. % Cr are cold worked, the magnetic susceptibility increases and weak ferromagnetism is observed.<sup>9</sup> This may be due to small distorted regions in the alloy that have been transformed from a hexagonal close-packed structure to a cubic one. Ferromagnetism is known to occur in cubic alloys containing about 25 at. % Cr in the Cr-Ir and in the Cr-Pt systems.<sup>10,11</sup> Although superconductivity does not occur in the Cr-Pt system (the  $\beta$ - $W$  type phase,  $\text{Cr}_3\text{Pt}$ , is not superconducting above 0.3°K), presumably due to the large homogeneity range of the ferromagnetic cubic phase, both superconductivity and ferromagnetism occur in the Cr-Ir system.

#### CHROMIUM-IRIDIUM SYSTEM

According to Raub and Mahler<sup>5</sup> there are three intermediate phases in this system. The  $\text{CrIr}_3$  phase has an ordered  $\text{Cu}_3\text{Au}$  type ( $L1_2$ ) structure and is ferromagnetic. The hexagonal close-packed alloy is superconducting above 0.3°K in the composition range of 60 to 75 at. % Cr. The maximum transition temperature occurs at 6.84 valence electrons/atom. The  $\text{Cr}_3\text{Ir}$  phase crystallizes in the  $\beta$ - $W$  type structure and has a homogeneity range from about 60 at. % Cr to about 90 at. % Cr. For an alloy containing 80 at. % Cr the transition temperature is 0.5°K and for a 90 at. % Cr alloy the

<sup>8</sup> E. Raub, *J. Less-Common Metals* **1**, 3 (1959).

<sup>9</sup> We should like to thank H. J. Williams and R. C. Sherwood for the magnetic measurements of these alloys.

<sup>10</sup> E. Friederich, *Z. tech. Physik* **13**, 59 (1932).

<sup>11</sup> A. Kussmann and E. Friederich, *Physik. Z.* **36**, 185 (1935).

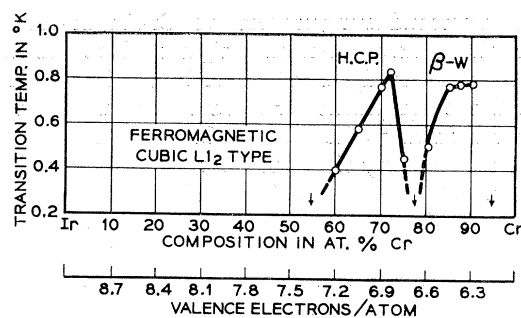


FIG. 3. Superconductivity in the Cr-Ir system.

transition temperature is 0.78°K. The solid solution of Ir in Cr is not superconducting above 0.3°K. The plot of the superconducting transition temperatures is shown in Fig. 3.

#### SUMMARY AND CONCLUSIONS

The occurrence of either superconductivity or ferromagnetism in the Cr-Ru, Cr-Rh, and Cr-Ir alloys seems to be associated to some extent both with the crystal structure of the phase and with the amount of Cr in the alloy. If the dilute Cr solid solution has an ordered cubic type structure, as in  $\text{CrIr}_3$ , it will be ferromagnetic. If, however, the structure is hexagonal close packed and the concentration of Cr is greater or less than the critical amount which appears necessary for ferromagnetic interaction, then the alloy will be superconducting. It has not been possible to date to observe the two structures and therefore the two phenomena in alloys with identical valence-electron concentrations. However, the cold-work experiments on the hexagonal close-packed Cr-Rh alloys offer some promise that this may be possible. As mentioned previously, the increase in magnetization may be due to a polymorphic change of isolated regions in the alloy from a hexagonal close-packed structure to a cubic one which causes a change from superconductivity to ferromagnetism in the alloy.

In all three Cr systems the hexagonal close-packed phase is superconducting which is similar to the corresponding superconducting Mo alloys. However, the transition temperature is somewhat lower because although Cr has lost most of its magnetic character in the hexagonal close-packed alloys with sufficient Cr concentration, either a small amount remains or there is a shift due to the intrinsic difference between the 3d Cr and 4d Mo solute atoms.

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