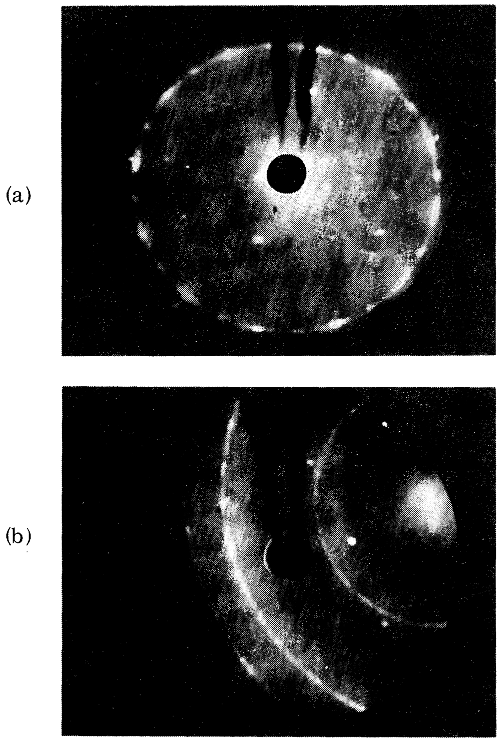

FIG. 3. Segmented ring (a) and completed ring (b) "disorder" surface structures of the (100) face formed after heating the crystal in the range $T = 750$–1769°C.

750°C in oxygen resulted in the appearance of the ring structure. Both surface structures appear to be unaffected by the presence of oxygen.

The platinum surface which exhibits the domain structure was heated in hydrogen ($\approx 2 \times 10^{-6}$ Torr) at 500°C. This treatment had no effect upon the diffraction pattern. The ring structure appeared when the crystal was heated in hydrogen at higher temperatures (>750°C).

Changing the conditions used for ion bombardment (argon, xenon, ion voltage, ambient pressure) had no effect upon the surface characteristics. The ring structure was also obtained without ion bombardment by heating the crystal to temperatures $T > 750$°C. The domain structure could not be obtained without ion bombardment. Heating the crystals to a temperature which corresponds to the stability range of the observed domain structure was inadequate to anneal the surface damage produced by our crystal preparation.

Using several crystals in all our experiments has not affected the reproducibility of the results. Therefore, it appears unlikely that impurities may be the cause of the observed surface structures.

Detailed investigations of these surface structures, of their kinetics of formation, are in progress and will be reported later. The catalytic properties of platinum and the temperature sensitivity of the catalytic activity[6] seems also to support our findings of the existence of different surface structures as a function of the thermal history of platinum single crystals.

We are indebted to Professor D. H. Templeton for helpful discussions.

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INSULATING FERROMAGNETIC SPINELS

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All previously known magnetic compounds having the spinel structure, except for one single compound, have spontaneous moments which are consistent with ferrimagnetic or more complex spin configurations. We report herein a family of chalcogenide spinels, typified by the compounds $CdCr_2S_4$, $CdCr_2Se_4$, $HgCr_2S_4$, and $HgCr_2Se_4$, which are both electrical insulators and ferromagnetic. The pertinent characteristics of these ferromagnetic compounds are given in Table I (all data taken on polycrystalline samples). The data for the similar compounds $ZnCr_2S_4$ and $ZnCr_2Se_4$, which are antiferromagnets, are also included in Table I for

Table I. Summary of crystallographic and magnetic characteristics.

Composition	Lattice parameter (Å)	U parameter	Magnetic moment (4.2°K) (μ_B/molecule)	Curie temperature T_C(°K)	Curie Weiss θ(°K)	Curie constant C_M	$\frac{\theta}{T_c}$
$Cd[Cr_2]S_4$	10.244	0.390	5.2	97	+135	3.2	1.39
$Cd[Cr_2]Se_4$	10.755	0.390	5.4	142	+190	3.67	1.34
$Hg[Cr_2]S_4$	10.237	0.390	5.3	60	+137	3.62	2.28
$Hg[Cr_2]Se_4$	10.753	0.390	5.4	120	+192	3.34	1.60
$Zn[Cr_2]S_4$	9.988	0.385	...	$TN < 20$	+18[a]	3.34[a]	...
$Zn[Cr_2]Se_4$	10.443	0.384[b]	...	$TN \simeq 20$[a]	+115[a]	3.54[a]	...

[a] Measurements of F. K. Lotgering, Philips Res. Rept. 11, 190, 337 (1956); and reference 2.

[b] Measurements of R. Plumer, Compt. Rend. 260, 3348 (1965).

contrast.

In all the compounds in Table I the Cr^{3+} ions on the six-coordinated sites of the spinel lattice are the only magnetic ions present. However, only the compounds with Cd^{2+} and Hg^{2+} on the four-coordinated sites have a magnetic moment close to the theoretical value of 6 μ_B/molecule for a ferromagnetic spin configuration. The temperature dependence of the magnetic moment and inverse susceptibility of $CdCr_2Se_4$, shown in Fig. 1, is typical of these compounds. Except for $HgCr_2S_4$, the ratios θ/T_C closely bracket the theoretical[1] value of 1.51 for Cr^{3+} on the six-coordinated sites of the spinel lattice. The observed Curie constants for all the compounds in Table I are close to the theoretical value of 3.75.

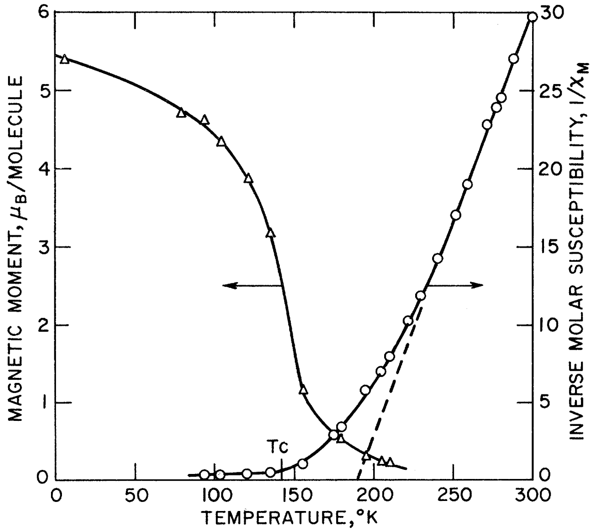

FIG. 1. Magnetic moment and inverse susceptibility of $CdCr_2Se_4$ for an applied field of 10 000 Oe.

The data of Table I indicate that the Curie temperatures of these compounds are very sensitive to substitution of the nonmagnetic cation on the four-coordinated sites. In the sulfide spinels ($CdCr_2S_4$ and $HgCr_2S_4$), as well as in the selenides ($CdCr_2Se_4$ and $HgCr_2Se_4$), the compounds containing Cd^{2+} and Hg^{2+} ions have essentially identical structural parameters, magnetic moments, and Curie-Weiss θ's, but have large differences in their ferromagnetic ordering temperatures. It was also observed that, whereas $CdCr_2S_4$, $CdCr_2Se_4$, and $HgCr_2Se_4$ are typical ferromagnets, the magnetic behavior of $HgCr_2S_4$ is more complex. Below 25°K, $HgCr_2S_4$ is an antiferromagnet at low fields and a ferromagnet at high fields (metamagnetic). Above 25°K its properties are those of a typical ferromagnet, in both low and high fields.

Other compounds such as $CuCr_2Se_4$ have been reported by Lotgering[2] and Blasse[3] as being ferromagnetic. However, the case for ferromagnetism or ferrimagnetism in $CuCr_2Se_4$ hinges on the coexistence of either Cu^{1+}-Cr^{4+} or Cu^{2+}-Cr^{3+} pairs, respectively, and an unambiguous distinction between these two possibilities has not yet been made. $LiZn_{0.5}Mn_{1.5}O_4$, also reported by Blasse,[3] is the only previously known compound with the spinel structure which is unquestionably a ferromagnet. It is noteworthy that the ferromagnetically aligned Mn^{4+} ions in this compound are isoelectronic with the Cr^{3+} ions of the ferromagnetic compounds herein reported.

In addition to being ferromagnetic, $CdCr_2S_4$, $CdCr_2Se_4$, $HgCr_2S_4$, and $HgCr_2Se_4$ are all electrical insulators. For example, $CdCr_2Se_4$ has a resistivity of 5×10^{15} Ω cm at 77°K and has conventional semiconducting properties in both ferromagnetic and paramagnetic states. The above-mentioned transport properties are in sharp contrast to the metalliclike conductivity of such compounds as $CuCr_2Se_4$, which certainly now cannot be argued as a necessary condition for ferromagnetism in the spinel structure.

Complete reports on the preparation and characterization of this new family of ferromagnetic spinels are in preparation.

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[1] From the high-temperature expansion of the susceptibility based on nearest neighbor ferromagnetic interactions only (P. J. Wojtowicz, private communication).

[2] F. K. Lotgering, Solid State Comm. 2, 55 (1964); *Proceedings of the International Conference on Magnetism, Nottingham, England, 1964* (The Institute of Physics and the Physical Society, University of Reading, Berkshire, England, 1965), p.533.

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METASTABLE CURRENT-CARRYING STATES OF WEAKLY COUPLED SUPERCONDUCTORS*

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The relative phases of the energy gaps of two superconductors separated by a thin insulating-junction layer are coupled by the tunneling interaction.[1-4] This interaction mixes configurations containing different relative numbers of pairs on the two sides of the junction, and the configuration mixing energy can be positive or negative depending on the relative difference of gap phase φ across the junction. Josephson[1] showed that this phase coupling leads to the possibility of a supercurrent flow of pairs across the insulating region. A doubly connected region (loop) consisting of one or more superconductors connected by one or more insulating junctions forms what we shall call a weakly coupled superconductor. Since the strength of the superconducting coupling across the junction varies exponentially with the thickness of the insulator, such a system provides in principle the possibility of studying the decay of supercurrent metastable states.[5] Here we report experimental and theoretical observations relating to the metastable current-carrying states of such weakly coupled superconducting loops.

The nature of these metastable states can be illustrated by considering a thick superconducting loop containing one insulating junction. The zero-temperature results which we give may be simply generalized to finite T. If the junction is characterized by the critical current I_1 which it can support, then the energy coupling the phases across the junction is $-(\hbar I_1/2e)\cos\varphi$. Throughout this discussion we assume that the junction dimensions are small compared to the Josephson penetration depth $\lambda_J = [\hbar c^2/8\pi e J_1(2\lambda+\delta)]^{1/2}$ so that the current is uniform over the junction area. Here λ is the penetration depth of the superconductor, J_1 is the current per unit area through the junction, and δ is the insulator thickness. For a loop of inductance L, the energy associated with a current I is

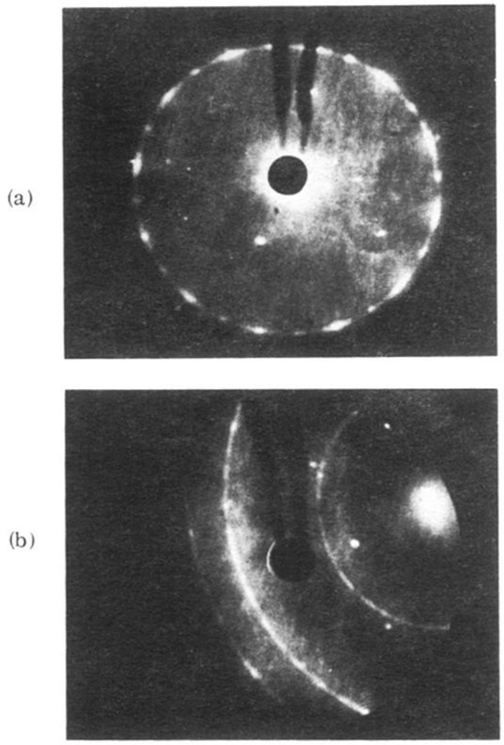
$$E = -\frac{\hbar I_1}{2e}\cos\varphi + \tfrac{1}{2}LI^2. \tag{1}$$

The first term is just the phase-coupling energy and the second the magnetic energy. For a thick loop, the continuity of phase around the loop implies

$$\varphi = \frac{-2e}{\hbar c}\int_{(\text{path})}\vec{A}\cdot d\vec{l}, \tag{2}$$

where the path stays in the interior of the superconductor and goes from one side of the junction to the other. For the junctions of interest, the additional contribution to the phase integral obtained by extending the path across the junction is negligible, so that

$$\varphi = -2\pi\frac{cLI}{\Phi_0} + 2n\pi. \tag{3}$$



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