

July 11, 1972

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3,676,082

MAGNETIC COMPOSITIONS

Filed May 19, 1967

2 Sheets-Sheet 1

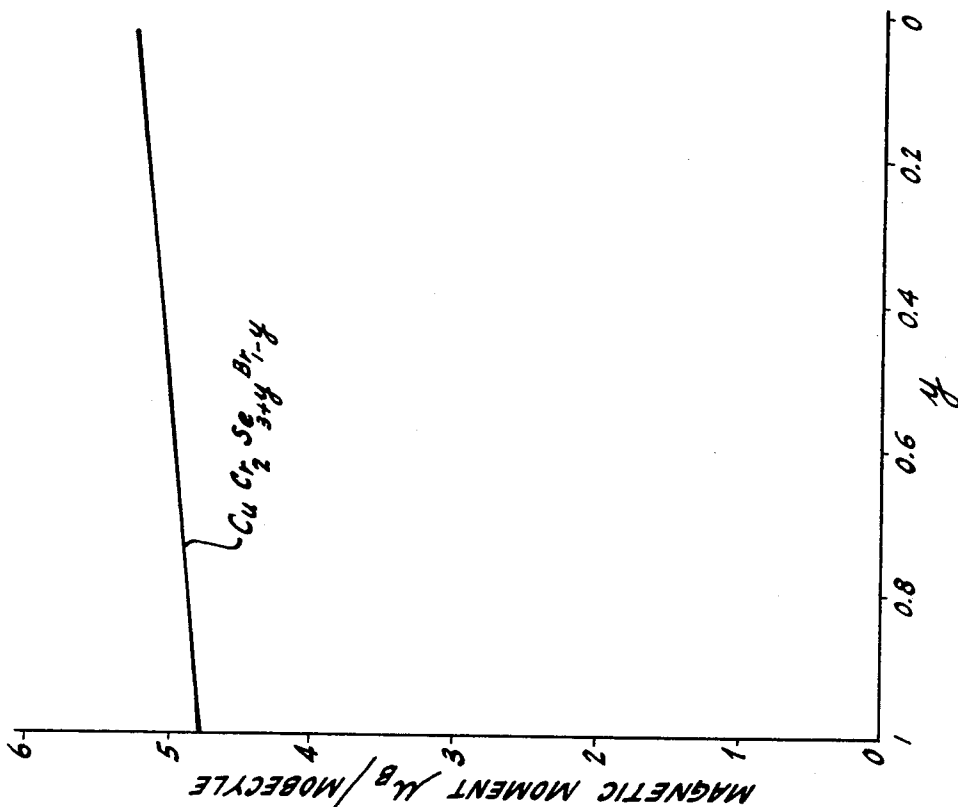


Fig. 2.

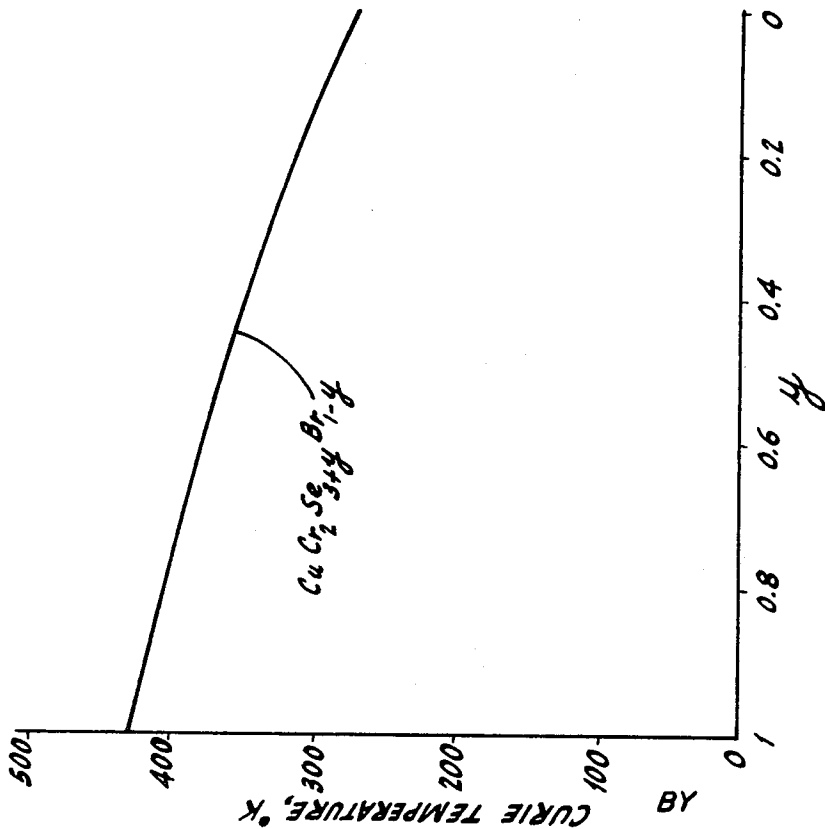


Fig. 1.

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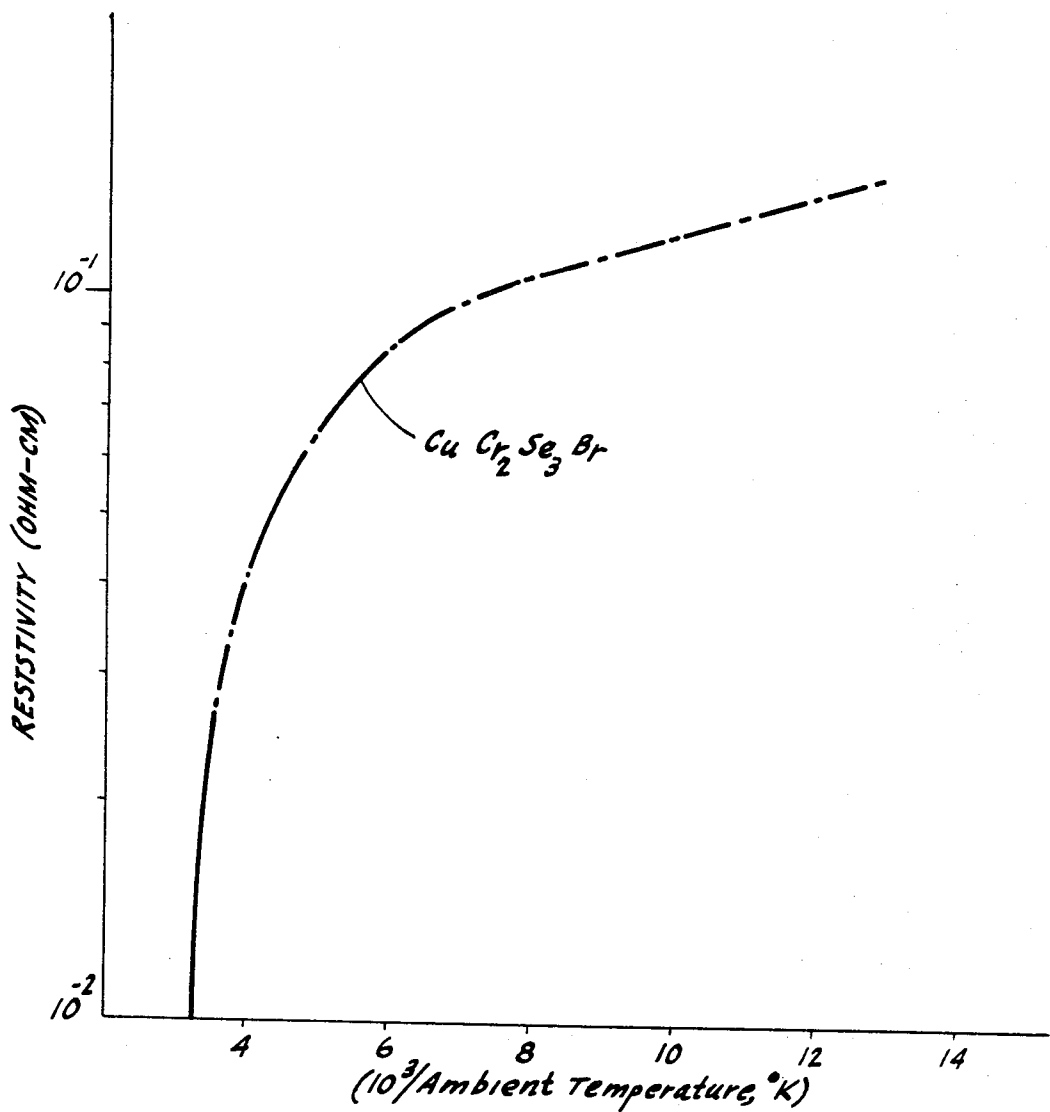


Fig. 3.

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1

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MAGNETIC COMPOSITIONS

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9 Claims

ABSTRACT OF THE DISCLOSURE

A new magnetic material comprises the molar formula $MM'Z_{3+y}X_{1-y}$ where: Z consists essentially of at least one of the chalcogenides, S^{2-} , Se^{2-} , Te^{2-} ; X consists essentially of at least one of the halides, Cl^- , Br^- , I^- ; M consists essentially of copper ions; M' consists essentially of chromium ions; and y is a number from zero to less than 1. Values of y exist above which the material behaves as a conductor and at or below which the material behaves as a semiconductor. The compositions are generally in the spinel crystal class and are useful in magnetic and semiconductor devices. A method of preparing the above material comprises first mixing the starting materials copper halide, chromium, chalcogen and copper in the molar ratios to give the desired product. Then pressed pellets of the mixture are formed and placed in evacuated quartz tubes. The pellets are then fired for at least 10 hours at 700-800° C.

BACKGROUND OF THE INVENTION

This invention relates to a new magnetic material useful in magnetic devices, semiconductor devices and devices requiring the combination of semiconductor and magnetic properties. More particularly, it relates to magnetic materials some of which are semiconductors having Curie temperatures near or above room temperature.

Materials having both magnetic and semiconducting properties are known in the art. These prior art materials have low Curie temperatures and therefore require cooling means for maintaining the materials below their Curie temperatures. For example, the compounds of gadolinium selenide and yttrium gadolinium selenide disclosed by S. J. Methfessel et al. in U.S. Pat. No. 3,271,709 have Curie temperatures of from about 55° K. to 80° K. The compounds $CdCr_2Se_4$ and $CdCr_2S_4$, reported to be ferromagnetic semiconductors by P. K. Baltzer et al. in Physical Review Letters 15, 493 (1965), have Curie temperatures of 84° K. and 130° K. respectively. Since magnetic materials are nonmagnetic above their Curie temperature, it is desirable to obtain materials with as high a Curie temperature as possible. Magnetic materials having higher Curie temperatures require less cooling or no cooling. This reduces or eliminates the requirements for cooling and reduces the cost of operating devices employing magnetic materials.

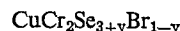
SUMMARY OF THE INVENTION

The novel magnetic materials described herein are characterized in that they have Curie temperatures near or above room temperature. These novel materials are believed to include the only presently known materials having the combined properties of a magnetic material and a semiconductor which in addition have Curie temperatures above room temperature.

The novel magnetic materials have the molar formula $MM'Z_{3+y}X_{1-y}$ wherein Z consists essentially of at least one of the chalcogenides, S^{2-} , Se^{2-} , and Te^{2-} , and X

2

consists essentially of at least one of the halides, Cl^- , Br^- and I^- . M and M' consist essentially of copper and chromium ions respectively. The value of y is a number from zero to less than 1. Values of y exist above which the magnetic materials are conductors and at and below which they are semiconductors. For example, in the series of materials represented by the formula



when y is between zero and about 4.5 the material behaves as a semiconductor. That is, its resistivity decreases with increasing temperature as measured for example from liquid nitrogen temperature to greater than room temperature. When y is a number greater than about 0.45 the material behaves as a conductor. That is, the resistivity increases with increasing temperature over the same temperature range.

The magnetic conductors are compatible with the magnetic semiconductors disclosed herein, and may be useful as conductive contacts to the semiconductor. For example, in a sandwich type structure.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph indicating the Curie temperature of the novel magnetic materials represented by the molar formula $CuCr_2Se_{3+y}Br_{1-y}$ as y varies from 0 to 1.

FIG. 2 is a graph indicating the magnetic moment of magnetic materials in the series $CuCr_2Se_{3+y}Br_{1-y}$ as y varies from 0 to 1.

FIG. 3 is a graph of the resistivity of $CuCr_2SeBr$ as a function of temperature showing the semiconductor behavior of this compound.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The novel magnetic materials are generally single phase structures of the spinel type. Typically, these materials are prepared by reacting copper halide, chromium, chalcogen and copper, or for the compounds resulting when y=0, by reacting CuX and Cr_2Z_3 , in an evacuated quartz tube at about 700-800° C. CuX represents copper iodide, copper bromide, or copper chloride. Cr_2Z_3 represents chromium sulfide, chromium selenide, or chromium telluride. The reactants are weighed and mixed such that the molar ratios of the elements in the reactant mixture is equal to the molar ratios of the elements in the desired product. The reactants are mixed together by dry milling for several hours. The milled reactants are then pressed into pellets which are sealed in evacuated quartz tubes. The pellets are then fired for at least about 10 hours. When it appears after the firing step that all of the reactants have not been converted to the final product it may be desirable to remove the pellets after the first firing, grind them into a powder, repress new pellets and refire them.

EXAMPLE 1

Magnetic $CuCr_2Se_3Br$ is prepared by weighing 0.05 mole of CuBr powder, 0.1 mole of Cr metal powder and 0.15 mole of Se powder and placing these materials together in a ball mill. The materials are mixed by dry milling for about 18 hours. The mixed powders are then placed in an apparatus for forming pellets from powder samples by pressing. Pellets are pressed from the powder using a pressure of at least about 5000 p.s.i. These pellets which are about $\frac{7}{16}$ inch in diameter and about from 1-2 inches long, are then placed in quartz tubes which are closed at one end. Usually, there is one pellet per tube. Each quartz tube is then evacuated and sealed at the other end while evacuated so as to form an ampoule

3

containing the pellet. The ampoule is then placed in a furnace and the temperature of the furnace is slowly (5–15° C. hr.) brought to the firing temperature of about 750° C. The furnace is held at this temperature for about 48 hours and then turned off and allowed to cool to room temperature. The fired pellets produced by this procedure have the empirical formula $\text{CuCr}_2\text{Se}_3\text{Br}$ and have a spinel structure with a lattice parameter a_0 of 10.42 Å, as determined by X-ray diffraction. The Curie temperature, T_c , of the final product is about 275° K.

EXAMPLE 2

Magnetic $\text{CuCr}_2\text{Se}_{3.4}\text{Br}_{0.6}$ is prepared by dry milling a mixture containing 0.03 mole of CuBr powder, 0.1 mole of Cr metal powder, 0.17 mole of elemental Se powder and 0.02 mole of Cu metal powder, for about 15 hours. The milled mixture is then pressed into pellets, sealed in an evacuated quartz ampoule and fired as described in Example 1. The Curie temperature, T_c , of the final product is about 345° K.

EXAMPLE 3

Magnetic $\text{CuCr}_2\text{Te}_3\text{I}$ is prepared by dry mixing a mixture containing 0.05 mole of CuI powder and either 0.1 mole of Cr metal powder and 0.15 mole of Te powder or 0.05 mole of Cr_2Te_3 powder, for about 18 hours. The milled mixture is then pressed into pellets, sealed in the evacuated quartz ampoule and fired as described in Example 1. The Curie temperature of this material is about 294° K.

EXAMPLE 4

Magnetic $\text{CuCr}_2\text{Te}_{3.2}\text{I}_{0.8}$ is prepared by dry milling a mixture containing 0.04 mole of CuI powder, 0.1 mole of Cr metal powder, 0.16 mole of Te powder and 0.01 mole of Cu metal powder, for about 18 hours. The milled mixture is then processed as described in Example 1. The Curie temperature of this material is about 307° K.

EXAMPLE 5

Magnetic $\text{CuCr}_2\text{Se}_3\text{Cl}$ is prepared by dry milling a mixture containing 0.05 mole of CuCl powder, 0.1 mole of Cr metal powder and 0.15 mole of Se powder, for about 18 hours. The milled mixture is then processed as described in Example 1.

Other compounds such as $\text{CuCr}_2\text{Te}_3\text{Br}$ and $\text{CuCr}_2\text{S}_3\text{Br}$ have been prepared by similar procedures. Also, the process has many variations which may be used to prepare the novel composition. For example, it is not necessary to dry mill, milling can be performed in a non-aqueous solvent provided the powder is properly dried prior to pressing and/or firing. Also, the milling time is not critical but should preferably be greater than about 4 hours.

Although it is preferred to form pressed pellets from the mixed powder, this step is not necessary. However, if pellets are not formed prior to firing the time of firing and number of firings required to convert all the reactants to the desired product may be increased. The pressure used to press the pellets is not critical but should be at least great enough to give a mechanically sound pellet.

Firing in a sealed tube is a convenient way of maintaining the partial pressures of volatile components of the reactants and preventing loss of any component. Where the tube is not sealed it may be difficult to control the composition of the final product as the volatile components may be depleted. The sealed tube is preferably evacuated but may contain inert gases.

The slow temperature rise of the furnace is merely a safety precaution to prevent explosion of the ampoule to the exothermic heat of reaction. The firing temperatures should be between about 700 to 800° C. and preferably

4

from about 750 to 800° C. with firing times of at least about 10 hours.

The Curie temperatures, T_c , of several of the novel compositions are shown in FIG. 1. The Curie temperatures of the materials represented by the formula $\text{CuCr}_2\text{Se}_{3+y}\text{Br}_{1-y}$ increases steadily from $T_c=275^\circ\text{K}$. when $y=0$ to $T_c=430^\circ\text{K}$. when $y=1$. The compound CuCr_2Se_4 , obtained when $y=1$, is metallic. The Curie temperature at $y=0.45$, which is the composition near which the material changes from a semiconductor to a conductor or metal, is about 355° K.

The magnetic strength of the novel materials represented by the molar formula $\text{CuCr}_2\text{Se}_{3+y}\text{Br}_{1-y}$ is shown in FIG. 2. The magnetization of these materials increases as the value of y decreases and is highest for the semiconducting compound $\text{CuCr}_2\text{Se}_3\text{Br}$. The resistivity of this compound as a function of temperature is shown in FIG. 3. The semiconducting behavior (an increase in resistivity with a decrease in temperature) is shown in the figure.

The table shows the resistivity of various compositions at room temperature and at liquid nitrogen temperature.

Composition	$\rho_{298^\circ\text{K}}$ (—cm.)	$\rho_{77^\circ\text{K}}$ (—cm.)	Nature of conduction
$\text{CuCr}_2\text{Se}_3\text{Br}$	13.2	185	Semiconductor.
$\text{CuCr}_2\text{Se}_{3.2}\text{Br}_{0.8}$	2	22	Do.
$\text{CuCr}_2\text{Se}_{3.4}\text{Br}_{0.6}$	0.78	2.4	Do.
$\text{CuCr}_2\text{Se}_{3.6}\text{Br}_{0.4}$	0.140	0.020	Metal.
$\text{CuCr}_2\text{Te}_3\text{I}$	8.8×10^{-3}	12×10^{-3}	Semiconductor.

The particular value of y , in the molar formula $\text{CuCr}_2\text{Z}_{3+y}\text{X}_{1-y}$, above which the compositions change from a semiconductor to a metal may be different for different combinations of chalcogenide (Z) and halide (X). The preferred maximum value of y is about 0.95. Above this value the change in magnetic moment is not considered significant.

What is claimed is:

1. A magnetic material consisting of a copper chromium chalcogenide halide represented by the molar formula $\text{CuCr}_2\text{Z}_{3+y}\text{X}_{1-y}$ wherein

(a) Z consists essentially of at least one chalcogenide selected from the group consisting of S^{2-} , Se^{2-} , and Te^{2-} ,

(b) X consists essentially of at least one halide selected from the group consisting of Cl^{1-} , Br^{1-} , and I^{1-} , and

(c) y is a number from zero to less than 1.

2. The magnetic material described in claim 1 wherein y is a number from zero to 0.95.

3. A magnetic semiconductor material consisting of a copper-chromium chalcogenide halide represented substantially by the molar formula $\text{CuCr}_2\text{Z}_{3+y}\text{X}_{1-y}$ wherein

(a) Z is at least one chalcogenide selected from the group consisting of S^{2-} , Se^{2-} , and Te^{2-} ,

(b) X is at least one halide selected from the group consisting of Cl^{1-} , Br^{1-} , and I^{1-} , and

(c) y is a number from zero to a maximum value of less than 1, said maximum being that value above which the material behaves as a conductor.

4. The magnetic semiconductor material described in claim 3, wherein Z is Te^{2-} and X is I^{1-} .

5. The magnetic semiconductor material described in claim 3 wherein y is a number from zero to about 0.45.

6. The magnetic semiconductor material described in claim 5 wherein Z is Se^{2-} and X is Br^{1-} .

7. A single phase ferromagnetic semiconductor compound having a spinel crystal structure and represented by the molar formula $\text{CuCr}_2\text{Se}_3\text{Br}$.

5

8. A single phase ferromagnetic semiconductor compound having a spinel crystal structure and represented by the molar formula $\text{CuCr}_2\text{Te}_3\text{I}$.

9. A magnetic material comprising a copper-chromium chalcogenide halide represented by the formula $\text{MM}'_2\text{Z}_{3+y}\text{X}_{1-y}$ wherein: 5

(a) Z consists essentially of at least one chalcogenide selected from the group consisting of S^{-2} , Se^{-2} , and Te^{-2} ,

(b) X consists essentially of at least one halide selected from the group consisting of Cl^{-1} , Br^{-1} , and I^{-1} , 10

(c) M consists essentially of copper ions,

(d) M' consists essentially of chromium ions, and

(e) y is a number from zero to less than 1.

6

References Cited

FOREIGN PATENTS

708,891 5/1965 Canada ----- 252—62.3 T

OTHER REFERENCES

Hahn et al.: Z. für Anorg. U. Allg. Chem. 303, pp. 107—112 (1960).

OSCAR R. VERTIZ, Primary Examiner

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U.S. Cl. X.R.

252—62.3 V, 62.51, 518