[1]H. Watanabe, Progr. Theoret. Phys. (Kyoto) 18, 405 (1957).

[2]H. Watanabe, Phys. Rev. Letters 4, 410 (1960).

[3]W. M. Walsh, Jr., Bull. Am. Phys. Soc. 4, 142 (1959).

[4]W. M. Walsh, Jr. and N. Bloembergen, Phys. Rev. 107, 904 (1957).

[5]W. M. Walsh, Jr., Phys. Rev. 114, 1473 (1959).

[6]W. Low, Proc. Phys. Soc. (London) B69, 1169 (1956).

[7]W. Low, Phys. Rev. 105, 793 (1957).

[8]W. M. Walsh, Jr. (unpublished).

[9]P. W. Bridgman, Proc. Am. Acad. Arts Sci. 67, 345 (1932).

[10]J. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) A247, 141 (1958).

[11]J. Lambe and C. Kikuchi, Bull. Am. Phys. Soc. 5, 158 (1960).

[12]W. M. Walsh, Jr., J. Jeener, and N. Bloembergen (unpublished).

EVIDENCE FOR AN ANTIFERROMAGNETIC-FERRIMAGNETIC TRANSITION IN Cr-MODIFIED Mn₂Sb

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We wish to report an unusual magnetization behavior found in the compound $Mn_{2-x}Cr_xSb_{1-y}In_y$, where $0.025 \leq x \leq 0.20$ and $0 \leq y \leq 0.05$. With decreasing temperature, the saturation magnetization undergoes a transition within about a 10° interval from a strongly ferrimagnetic state ($\sigma = 20$ to 30 gauss-cm³/g) to a weakly magnetic state ($\sigma \approx 1$ gauss-cm³/g). This transition, which occurs in the temperature range 120 to 385°K depending on the amount of chromium present, is not accompanied by a change in crystal structure. At high temperatures, the magnetic properties of these compounds are similar to those of the parent compound Mn_2Sb,[1] but the saturation magnetization is too low to be accounted for entirely by the amount of chromium and indium present. As the temperature is lowered, transition to the weakly magnetic state takes place. This behavior is illustrated in Fig. 1, where the saturation magnetization is plotted as a function of temperature for two compounds, $Mn_{1.87}Cr_{0.13}Sb_{0.95}In_{0.05}$ and $Mn_{1.95}Cr_{0.05}Sb_{0.95}In_{0.05}$. The saturation magnetization for Mn_2Sb is included for comparison.

Below the transition temperature T_S, the materials exhibit an average saturation magnetization of 1 gauss-cm³/g. Metallurgical studies have shown, however, that there is a tendency toward nonstoichiometry on the manganese-deficient side resulting in precipitation of a small amount of MnSb. If the modified Mn_2Sb is formed with excess manganese, the residual magnetization is reduced but not eliminated completely. We attribute this residual magnetization to ferromagnetic MnSb precipitate. It appears then that the compound of interest may have no net magnetic moment below the transition temperature. The

indium present in these compositions has but little effect on their magnetic properties and can in fact be eliminated without loss of the magnetic transition. However, in the absence of indium during the synthesis, it becomes even more difficult to avoid precipitation of MnSb.

The composition region in which ferrimagnetism occurs is designated by the cross-hatched area in Fig. 2. This area is bounded at high temperature by the normal Curie temperature and at low temperature by the transition at T_S. It is to be
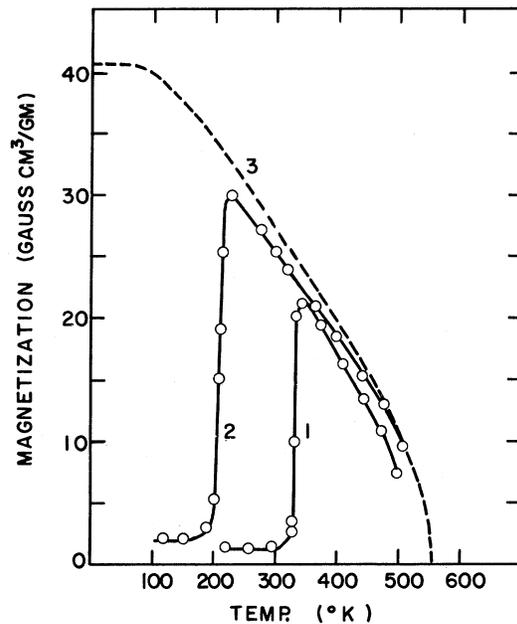

FIG. 1. Saturation magnetization of $Mn_{2-x}Cr_xSb_{1-y}In_y$. Curve 1, $x = 0.13$, $y = 0.05$; curve 2, $x = 0.05$, $y = 0.05$; curve 3, Mn_2Sb ($x = 0$, $y = 0$).
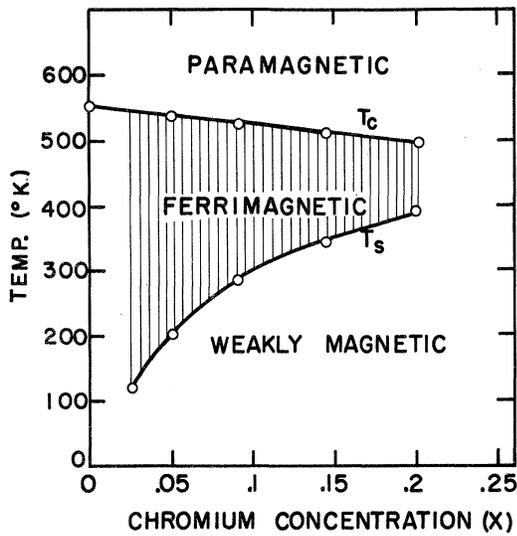
FIG. 2. Exchange inversion temperature T_S and Curie temperature T_C of $Mn_{2-x}Cr_xSb_{1-y}In_y$ as a function of x. Cross-hatched area defines temperature region in which compound is ferrimagnetic.
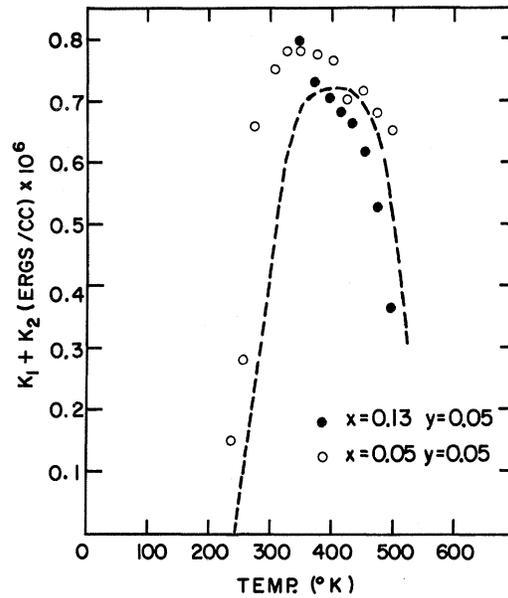

FIG. 3. The anisotropy constant, $K_1 + K_2$, of $Mn_{2-x}Cr_xSb_{1-y}In_y$ for two different amounts of Cr. The dashed curve represents the anisotropy of Mn_2Sb.

FIG. 4. c-axis dimension of $Mn_{2-x}Cr_xSb_{1-y}In_y$ as a function of temperature for various values of x and for Mn_2Sb ($x = 0$).

noted that the Curie temperature decreases slightly with the addition of chromium, but this decrease is small compared to the strong dependence of T_S on x.

Measurement of the magnetization curves with fields applied parallel and perpendicular to the tetragonal axis of a crystal shows that the compounds have a uniaxial magnetocrystalline anisotropy similar to that observed in Mn_2Sb. The anisotropy constant K, representing the difference in energy required to magnetize parallel and perpendicular to the tetragonal axis, is shown in Fig. 3. This anisotropy can only be measured in the ferrimagnetic region, but in three examples with different chromium content, $x = 0.13$, $x = 0.05$, and $x = 0$, K is virtually the same.

The crystal structure of these compounds is identical to that of Mn_2Sb [2] ($P4/nmm$) throughout the entire temperature range. X-ray studies of a single crystal with $x = 0.12$ and $y = 0.05$ show that the c axis of the unit cell contracts from 6.530 A to 6.516 A and that the a axes expand from 4.0875 A to 4.0882 A as the material is cooled through its magnetic transition at 50°C. This contraction leads to a net decrease in volume of approximately 0.18%. At the lowest temperature for which this compound remains ferrimagnetic, the c/a ratio is 1.598 compared to 1.608 for Mn_2Sb. The x-ray density, 7.04 g/cm³, is slightly greater than that of Mn_2Sb, 7.02. Figure 4 shows the behavior of the c-axis lattice
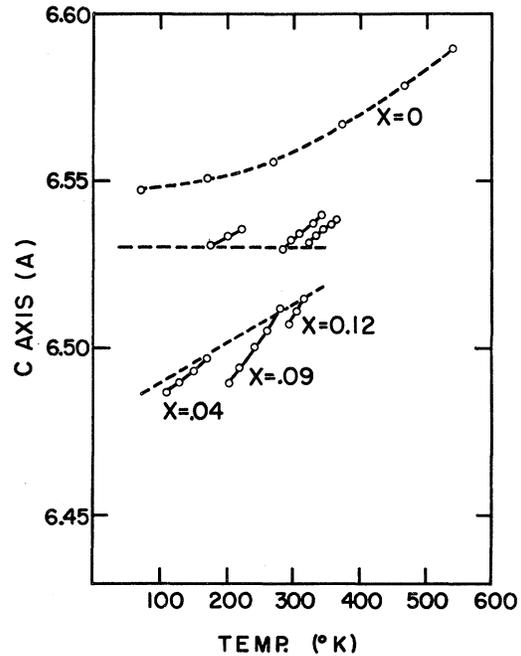
constant for several values of x. In all cases, the compounds transform to the weakly magnetic state for the same critical value of lattice constant.

Since it is unlikely that a transition from an ordered to a random state would occur with decreasing temperature, we propose that the low-temperature region possesses antiferromagnetic ordering rather than being paramagnetic. Preliminary results from neutron diffraction, obtained in cooperation with Battelle Memorial Institute, support this conclusion, and detailed results will be reported soon.

To account for the transition, we suggest that at least one of the exchange interactions changes sign near the critical dimension 6.53 A. Such a change in sign might occur because of possible opposing effects of certain superexchange and indirect exchange[3] interactions. It is not necessary to assume that a large change in either interaction must accompany the magnetic transition but only that their relative contribution is altered

by the contraction of the crystal near the critical c-axis dimension. We propose to designate this temperature as the "exchange inversion temperature."

The authors wish to thank Dr. J. J. Cox of the Engineering Research Laboratory for the results from his metallurgical studies and Dr. F. J. Darnell for the data on the anisotropy of Mn_2Sb reported here. Mr. Keith Babcock performed the x-ray measurements on the unit-cell dimensions.

[1]Charles Guillaud, thesis, University of Strasbourg, 1943 (unpublished).

[2]L. Heaton and N. S. Gingrich, Acta. Cryst. 8, 205 (1955).

[3]M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954).

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[111] DIRECT TRANSITION EXCITON AND MAGNETOREFLECTION IN GERMANIUM

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(Received April 14, 1960)

From theoretical considerations of the g factor of electrons in germanium[1,2] and infrared[3] and microwave[4] experiments, it was deduced that a direct transition at an energy of ~ 2 ev[5] exists between the $L_{3'}$ and L_1 bands at the edge of the Brillouin zone along the [111] direction. (See Fig. 1.) This suggests the possibility of carrying out reflection experiments at liquid helium temperatures with magnetic fields and high-resolution grating spectrometers that could provide information about the $L_{3'}$ valence band. Under these experimental conditions it would be possible to observe a third exciton in germanium consisting of the [111] electron and a [111] hole. In addition the magneto-reflection would permit the observation of the fine structure of the Zeeman effect of this [111] exciton and also the direct transition between Landau levels of the $L_{3'}$ valence and L_1 conduction bands along two sets of principal crystal directions. The information to be obtained by these experiments consists of the effective-mass parameters of the $L_{3'}$ holes, the g factor of both electrons and holes and their anisotropies, an accurate determination of the energy gap between the two bands, and a measurement of the binding energy of the exciton. The purpose of this Letter is to predict theoretically some of these quanti-

ties and to specify those pertinent aspects of the experiments required for obtaining the desired information.

If second order perturbation theory using the $\vec{k} \cdot \vec{p}$ technique is applied to the L_1 conduction band, it can be shown that the matrix elements between this and the $L_{3'}$ band are essentially those that
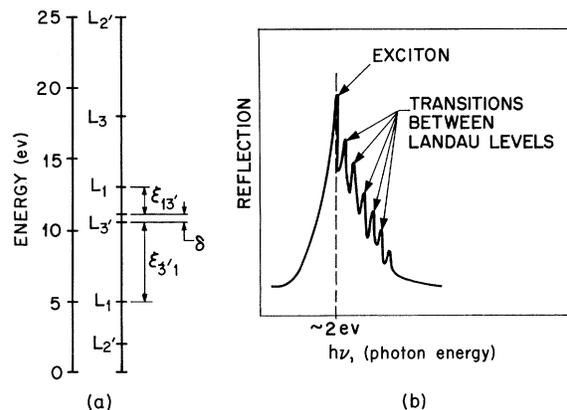

FIG. 1. (a) Approximate energy positions of band edges at the [111] zone edge in germanium. $\delta \approx 0.2$ ev is the spin-orbit splitting of the $L_{3'}$ band. (b) Sketch of expected [111] magnetoreflection spectrum. Fine structure is not indicated.