ANOMALOUS THERMOELECTRIC POWER OF $FeCr_2S_4$ NEAR THE CURIE TEMPERATURE

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(Received 22 June 1966)

An anomalous increase of the thermoelectric power in semiconducting, p-type $FeCr_2S_4$ is found near the Curie temperature. Analysis of the Fermi energy indicates that this effect is apparently due to an additional kinetic energy which the charge carriers acquire through magnon-hole interaction.

In a recent paper by Wasscher and Haas[1] the anomalous increase of the thermoelectric power, α, in semiconducting MnTe below its Néel temperature[2] is attributed to magnon drag.[3] This effect arises from a strong interaction between spin waves (magnons) and charge carriers through which additional carriers are dragged along a temperature gradient, thereby increasing α above the normal diffusion term. In order to fit the experimental data for MnTe to the magnon-drag model, a very short magnon-carrier relaxation time of $\sim 10^{-15}$ sec had to be assumed.[1]

We wish to report in this Letter an anomalous thermoelectric power increase, similar to the one found in MnTe, which we observed in single crystals of $FeCr_2S_4$. $FeCr_2S_4$ is known to be a semiconducting, normal spinel which becomes ferrimagnetic below 195°K.[4] The results of our measurements agree with the general picture of a p-type semiconductor and are shown in Fig. 1. At low temperatures, α increases with temperature T, in a way typical for extrinsic semiconductors. Between 160°K and the Curie temperature, α increases anomalously. The decrease of α at high temperatures is due to intrinsic conduction, as will be shown below.

If one calculates α vs T for an extrinsic, nondegenerate semiconductor and matches the curve between 120 and 160°K in Fig. 1, the thermoelectric power should follow the broken line. The additional thermoelectric power above 160°K, therefore, is likely to be due to the magnetic nature of $FeCr_2S_4$. To analyze our data further, we write the general expression of α for a p-type semiconductor,

$$\alpha = (1/eT)(E_F + E_K), \quad (1)$$

where e is the electron charge, E_F is the Fermi energy, and E_K is the kinetic energy of the holes. For a broad-band semiconductor it is usually assumed[5] that E_K is of the order of the thermal energy, kT (where k is Boltzmann's constant). We assume the same to be the case for $FeCr_2S_4$, since Hall measurements indicate band conduction below 200°K (Hall mobilities of the order of 10 cm^2/V sec near 110°K). A plot of $\alpha T - kT$ vs T will then give the temperature dependence of the Fermi energy in eV. The results of such a calculation with the data of Fig. 1 are shown in the upper curve of Fig. 2. This curve exhibits two interesting features. At high temperatures, above 400°K, the Fermi energy levels off, indicating intrinsic conduction. This conclusion is further sup-

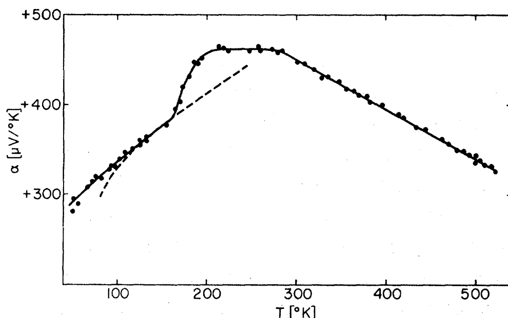

FIG. 1. Thermoelectric power α as a function of temperature T for $FeCr_2S_4$ single crystal.

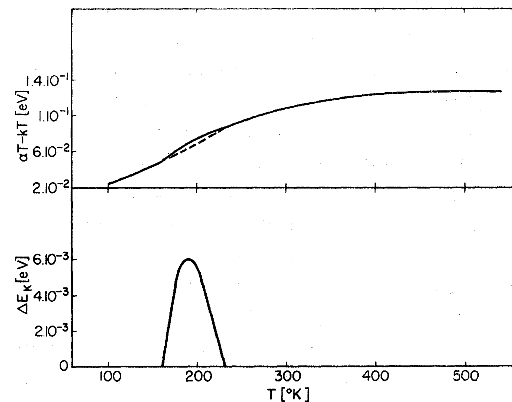

FIG. 2. Upper part: Fermi energy as function of temperature T calculated from data of Fig. 1. Lower part: Additional kinetic energy ΔE_K acquired by holes near Curie temperature T_C.

ported by the electrical conductivity which increases in this temperature region exponentially with an activation energy of 0.29 eV.

A second interesting feature of Fig. 2 is a bump in E_F vs T near the Curie temperature. An anomalous increase of E_F at a given temperature could only arise from an increase of the effective mass m^* due to band narrowing in approaching T_C. Although such behavior is conceivable,[6] the E_F vs T curve should not show in this case two points of inflection near T_C, since this would mean that m^* after an initial increase decreases again. We are, therefore, inclined to assume that around T_C the curve of E_F vs T is not a true reflection of the behavior of the Fermi level. Instead, we propose that the charge carriers acquire in this temperature region an additional kinetic energy, ΔE_K, due to a magnon-hole interaction. If we calculate the difference between the original curve of Fig. 2 and a smooth curve drawn along the broken line shown in the figure, we obtain this additional kinetic energy as a function of temperature. The result of this calculation is plotted in the lower part of Fig. 2. At the Curie temperature ΔE_K reaches a maximum and falls off rapidly towards higher and lower temperatures. This behavior is qualitatively consistent with the magnon-drag model since the magnon-carrier relaxation time becomes extremely short when approaching T_C from lower temperatures.[1] That ΔE_K does not disappear abruptly at T_C is an indication of magnetic short-range order up to approximately 230°K.

Although the above analysis shows a qualitative agreement of our data with the magnon-drag model, a final proof can only come through a quantitative comparison. For this we need to know the magnon-magnon and magnon-hole relaxation times, which we cannot derive from the present measurements. Further detailed electrical transport measurements are in progress.

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DIRECT OBSERVATION OF LITHIUM-DEFECT INTERACTION IN SILICON BY ELECTRON PARAMAGNETIC RESONANCE MEASUREMENTS*

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(Received 14 June 1966)

Electron paramagnetic resonance measurements have been used to observe directly the interaction of lithium with damage centers produced by electron irradiation in n-type, float-zone silicon. The silicon is characterized by low oxygen concentrations, with lithium as the predominant n-type dopant. Low oxygen concentrations might be expected to foster the interaction of lithium with radiation-induced defects on two counts: (1) Since in silicon containing ~$10^{18}/\mathrm{cm}^3$ oxygen the shallow lithium donor is really a (Li-O) complex, the absence of oxygen might make the isolated lithium[1] more mobile and/or susceptible to trapping by other imperfections and defects; (2) the absence of oxygen removes the possibility of forming oxygen-vacancy complexes (A centers),[2] thus increasing further the likelihood of lithium interacting with vacancies.

Float-zone silicon with quoted oxygen concentrations of $(1\text{-}2)\times10^{15}/\mathrm{cm}^3$ and a resistivity of 12 Ω cm (n type) was diffused with lithium from a Li-Sn alloy at 400°C to a resistivity of 0.3-0.4 Ω cm and a lithium concentration of about $2\times10^{16}/\mathrm{cm}^3$. The material was then bombarded by a 1-MeV electron flux of $1\times10^{16}/\mathrm{cm}^2$ at room temperature. The epr properties of the material were measured at 27°K using a Varian spectrometer operating at 9.1 kMc/sec. The major result of our preliminary work is the finding of a new lithium damage-center complex with a relatively high introduction rate which has not heretofore been reported.

The epr spectra of Fig. 1 illustrate our ba-