Electrical Resistivity and Hall Effect of Cr-Modified Mn_2Sb

P. E. BIERSTEDT
Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware*
(Received 12 June 1963)

Electrical resistivity has been measured as a function of temperature for single crystals of $Mn_{2-x}Cr_xSb$, where $0.01<x<0.2$. These materials exhibit exchange inversion transitions, and their resistivity at a given temperature depends almost entirely on the magnetic ordering and is essentially independent of the chromium concentration for temperatures greater than 100°K. These transitions are first order, and the thermal hysteresis associated with them decreases as the transition temperature increases. External magnetic fields lower the transition temperatures, and the extent of this decrease, $(\partial H/\partial T_s)_P$, is a function of the zero-field transition temperature. Hall effect measurements at room temperature indicate that the effective number of current carriers is 1.0 hole per molecule for compounds with either ferrimagnetic or antiferromagnetic ordering.

INTRODUCTION

IT has been reported that Cr-modified Mn_2Sb, $Mn_{2-x}Cr_xSb$, where $0.025\leq x\leq 0.20$, undergoes a ferrimagnetic to antiferromagnetic (F/AF) transition on cooling, the temperature of this transition being dependent on the chromium concentration.[1] Additional investigations have defined certain compositions with $0.023<x<0.035$ in which the F/AF transition occurs through a stable intermediate magnetic state (I), and other compositions with $x<0.022$ in which only the F/I transition occurs.[2] Resistivity measurements show that abrupt resistivity changes accompany these magnetic transitions, and the changes in resistivity with temperature for this system over the range 100 to 600°K have been published.[3] At the exchange inversion temperature for the F/AF transition, the resistivity rises sharply from the Mn_2Sb curve to an envelope of new curves associated with antiferromagnetic ordering. Further investigation, with special attention to the temperature range 4 to 100°K, has shown that there is also a characteristic resistivity associated with the intermediate magnetic state.[2]

Changes in electrical properties have been shown to be associated with magnetic changes in many materials. Resistivity measurements have been used in the investigation of magnetic changes in the rare-earth metals,[4] in $Mn_{1-x}Cr_xSb$,[5] and in the ordered alloy FeRh.[6] In Mn_2Sb, the temperature coefficient of resistance changes at the anisotropy inversion temperature,[3,7] and a change in this coefficient has also been measured at the Curie temperature.

This paper presents certain electrical properties of the $Mn_{2-x}Cr_xSb$ system and indicates how these properties are related to the unique magnetic behavior of this system. The transition temperatures and other parameters relating to the exchange inversion transitions, as obtained through resistivity measurements, are in excellent agreement with the values obtained by other techniques.

EXPERIMENTAL PROCEDURE

The compositions used in this investigation were grown as single crystals pulled from a melt of the elements in their proper proportions. The details of the method of preparation are given elsewhere.[8] Samples in the form of rectangular parallelepipeds with approximate dimensions 6 mm×2 mm×0.2 mm were cut from the single crystals.

Within the range of compositions studied, Cr-modified Mn_2Sb has a tetragonal crystal structure,[8] and the samples were oriented with the smallest dimension along the tetragonal axis. Since the presence of (001) cleavage planes made electrical measurements in other orientations difficult, all the electrical properties were measured with the current flowing in the basal plane. The samples were placed in a sample holder, and the necessary electrical leads plus a copper-constantan thermocouple were spot-welded to the samples using the capacitor-discharge technique. The leads were formed from small copper wire (3- to 5-mil diam), and strain-relief loops were provided to allow for changes in sample dimensions which result from the exchange-inversion transition as well as from thermal expansion and contraction. The sample holder was enclosed in a brass radiation shield which contained a wire heater noninductively wound along the entire length of the sample area.

Measurements from 77°K to room temperature were made in a gas cryostat consisting of a narrow-necked Dewar containing liquid nitrogen. The sample holder

* Contribution No. 833.

[1] T. J. Swoboda, W. H. Cloud, T. A. Bither, M. S. Sadler, and H. S. Jarrett, Phys. Rev. Letters **4**, 509 (1960).

[2] P. E. Bierstedt, F. J. Darnell, W. H. Cloud, R. B. Flippen, and H. S. Jarrett, Phys. Rev. Letters **8**, 15 (1962).

[3] H. S. Jarrett, P. E. Bierstedt, F. J. Darnell, and M. Sparks, J. Appl. Phys. **32**, 57S (1961).

[4] R. V. Colvin, S. Legvold, and F. H. Spedding, Phys. Rev. **120**, 741 (1960).

[5] T. Suzuoka, J. Phys. Soc. Japan **12**, 1344 (1957).

[6] J. S. Kouvel and C. C. Hartelius, J. Appl. Phys. **33**, 1343 (1962).

[7] C. Guillaud, Compt. Rend. **221**, 439 (1945).

[8] F. J. Darnell, W. H. Cloud, and H. S. Jarrett, Phys. Rev. **130**, 647 (1963).

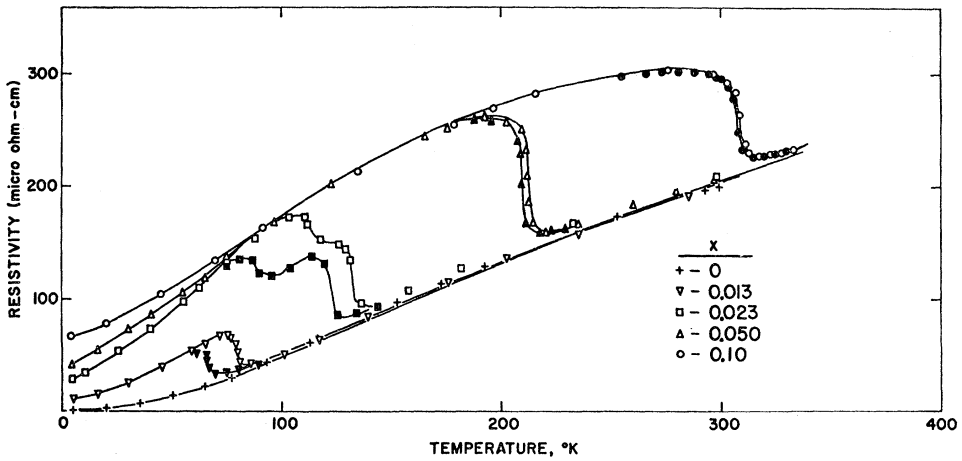

FIG. 1. Temperature dependence of the electrical resistivity of $Mn_{2-x}Cr_xSb$ for several values of x; data on warming and cooling (opened and closed symbols, respectively).

was placed in the neck of the Dewar above the level of the coolant. The coolant was evaporated by means of a second heater immersed in it, and the cold nitrogen gas flowing up the neck cooled the specimen. The temperature could be maintained constant within 0.5° by controlling the power input of these two heaters. The narrow neck of the Dewar was placed in the gap of a 4-in. Varian magnet for measurements of the effects of magnetic fields on the resistivity.

Below 77°K, measurements were made by transferring the sample holder to a liquid-helium Dewar, and the temperature was changed by moving the sample through the temperature gradient in the Dewar.

Resistance values were measured versus temperature by the potential-probe method, using an apparatus of the Dauphinee and Mooser design.[9] With this instrument, repeat measurements of the room-temperature resistance, after cooling to 77°K, gave agreement to within 1%. Resistance versus temperature curves were also obtained by an automatic recording technique. In this technique, a constant current was passed through the sample, and the voltage drop across the potential probes was amplified by a dc amplifier and applied to the Y axis of an X-Y recorder. The X axis recorded the temperature by measuring the output of a copper-constantan thermocouple. This latter technique was used exclusively to obtain the effects of magnetic fields on the exchange inversion transitions.

ELECTRICAL RESISTIVITY

Measurements of the electrical resistivity as a function of temperature were made on several $Mn_{2-x}Cr_xSb$ compositions ($0.01<x<0.2$) by the techniques outlined above. The resistivity versus temperature curves for several of these compounds and Mn_2Sb are given in Fig. 1. These curves show the resistivity changes that accompany the various exchange-inversion transitions occurring in this system, and Table I lists the transition temperatures of these compounds. The relation between transition temperature and composition for the entire composition range of these compounds is given graphically by Darnell *et al.*[8] From Fig. 1, it is seen that single transitions occur in $Mn_{1.987}Cr_{0.013}Sb$ (F/I), in $Mn_{1.950}Cr_{0.050}Sb$ (F/AF), in $Mn_{1.90}Cr_{0.10}Sb$ (F/AF), and that two transitions occur in $Mn_{1.977}Cr_{0.023}Sb$ (F/I and I/AF). In addition, it is observed that at 4°K the resistivities of these compounds depend not only on their magnetic state but also on their chromium content. At 4°K, the resistivity increases as the amount of chromium increases, but at temperatures near 100°K and above, the resistivity is essentially independent of the chromium content and is largely dependent on the type of magnetic ordering in the compound.

TABLE I. Transition temperatures for several $Mn_{2-x}Cr_xSb$ compounds.

Compound	Transition	Transition temperature (°K)
Mn_2Sb	No transition	
$Mn_{1.987}Cr_{0.013}Sb$	F/I	66
	I/F	80
$Mn_{1.977}Cr_{0.023}Sb$	I/AF	88
	AF/I	113
	F/I	123
	I/F	132
$Mn_{1.950}Cr_{0.050}Sb$	F/AF	209
	AF/F	212
$Mn_{1.90}Cr_{0.10}Sb$	F/AF	308
	AF/F	309

In the first-order transitions, shown in Fig. 1, thermal hysteresis is observed. If T_s^0 is defined as the transition temperature, in zero applied magnetic field, for the exchange-inversion transition occurring on cooling, then ΔT_s^0 is the thermal hysteresis associated with this transition. Since the transitions occur over a finite temperature interval, T_s^0 is taken as the temperature

[9] T. M. Dauphinee and E. Mooser, Rev. Sci. Instr. **26**, 660 (1955).

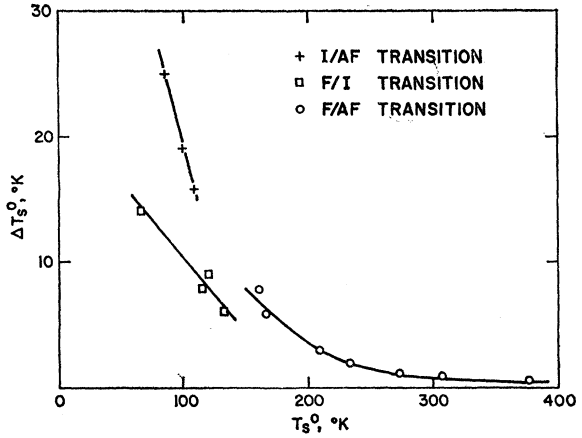

FIG. 2. Thermal hysteresis associated with the exchange inversion transitions in $Mn_{2-x}Cr_xSb$ versus transition temperature.

at which the transition is half-completed, or the midpoint of the transition. The values of ΔT_s^0 and T_s^0, taken from Table I and from results on other $Mn_{2-x}Cr_xSb$ compounds, are plotted in Fig. 2. A smooth curve can be drawn connecting the points between 150 and 370°K, representing the thermal hysteresis accompanying the F/AF transition. A discontinuity exists near 150°K where the F/AF transition becomes the double transition F/I and I/AF.

Electrical resistivity measurements have been made in external magnetic fields to determine the extent of the shift in the transition temperature with field. The advantages of using this technique to measure the exchange inversion transitions are the precision of the resistivity measurements, the degree of temperature control, and the proven correlation between electrical and magnetic properties. External magnetic fields were found to decrease the transition temperature T_s and after the material was saturated and the anisotropy field exceeded, the decrease was linear with field over the range studied. An example of such a shift in T_s in $Mn_{1.94}Cr_{0.06}Sb$ is shown in Fig. 3 for the magnetic field H oriented parallel to the c axis. From the high-field portion of this plot, $(\partial H/\partial T_s)_P$ was found to be -2.49 kOe deg^{-1} for the AF/F transition and -2.37 kOe deg^{-1} for the F/AF transition, a difference of less than 5%. Results were also obtained for the magnetic field oriented perpendicular to the c axis and the values agreed with those given above. From measurements of this type, values of $-(\partial H/\partial T_s)_P$ were obtained for several compositions, and for those involving only the F/AF and AF/F transitions the values of $-(\partial H/\partial T_s)_P$ are independent of the external field orientation, but vary with the transition temperature. The $-(\partial H/\partial T_s)_P$ values for the $Mn_{2-x}Cr_xSb$ system with $0.02<x<0.2$ are shown as a function of the transition temperature in Fig. 4. By using pulsed fields as large as 130 kOe,

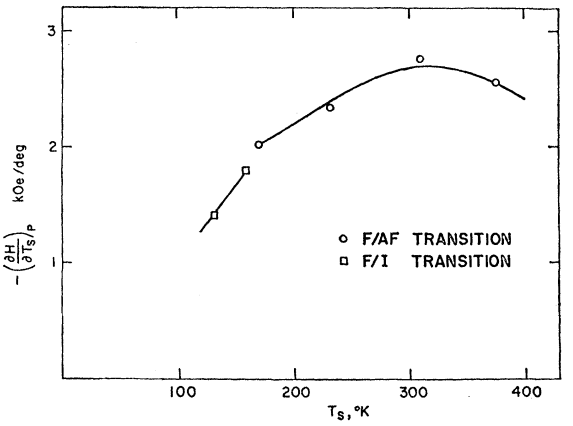

FIG. 4. Field coefficient $-(\partial H/\partial T_s)_P$ versus transition temperature for $Mn_{2-x}Cr_xSb$.

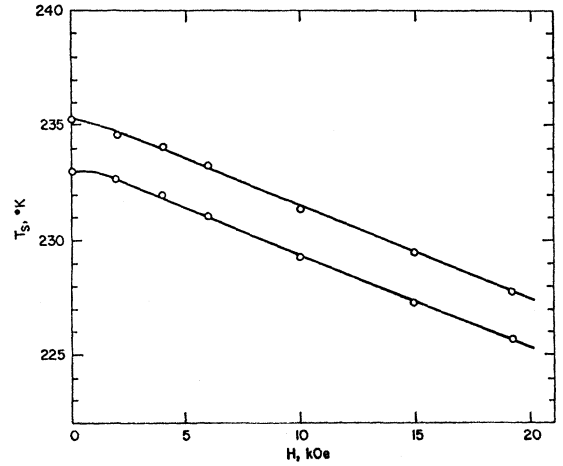

FIG. 3. Transition temperature of $Mn_{1.94}Cr_{0.06}Sb$ versus applied magnetic field oriented parallel to the c axis. Upper curve for AF/F transition, lower curve for F/AF transition.

Flippen and Darnell[10] have also obtained values of $(\partial H/\partial T_s)_P$ for these compositions. In view of the vastly different techniques and magnetic-field strengths employed, the agreement of approximately 10% is considered quite good. A complete treatment of these field coefficients and other thermodynamic properties of this system is given by Doerner and Flippen.[11]

Resistivity measurements in external magnetic fields have shown that, in certain Cr-modified Mn_2Sb compositions with T_s^0 less than in 150°K, both the magnitude and the orientation of the external field affect the exchange inversion transitions. The resistivity versus temperature curves for $Mn_{1.97}Cr_{0.03}Sb$ obtained in external fields of various strengths and two orientations are shown in Fig. 5. The fields were oriented either

[10] R. B. Flippen and F. J. Darnell, J. Appl. Phys. 34, 1094 (1963).

[11] W. A. Doerner and R. B. Flippen (to be published).

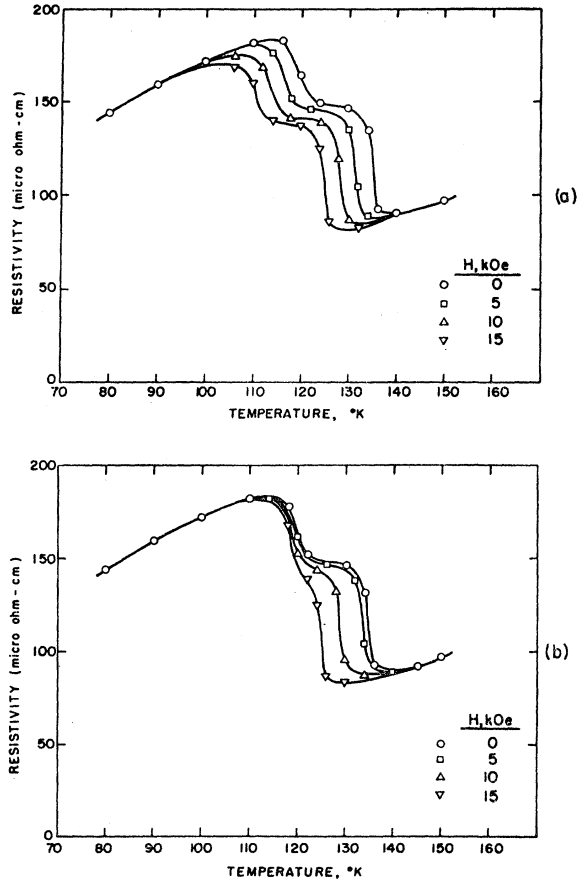

FIG. 5. Temperature dependence of the electrical resistivity of $Mn_{1.97}Cr_{0.03}Sb$ in applied magnetic fields of various strengths; (a) $H \perp c$ axis, (b) $H \parallel c$ axis. Transitions measured with increasing temperature.

perpendicular or parallel to the c axis, and the transitions were measured with increasing temperature. The differences between the effects caused by the two field orientations are most pronounced for the AF/I transition.

For the magnetic field aligned parallel to the c axis, the shift in the transition for a given field is much less than when the magnetic field is perpendicular to the c axis. Such behavior indicates a high-internal field, the alignment of which is only slightly influenced by moderate external fields ($\sim$20 kOe) parallel to the c axis. This observation is in agreement with those of Darnell *et al.*[8] who found a large crystalline anisotropy of the intermediate state, in which the moments are perpendicular to the c axis. The shift of the I/F transition is less dependent on the field orientation, but the effects of crystalline anisotropy are still evident.

HALL EFFECT

The change in resistivity accompanying exchange inversion transitions in Cr-modified Mn_2Sb can be attributed to the difference in the magnitude of the scattering of the conduction electrons by the ferrimagnetic and antiferromagnetic magnons, or to a change in the number of current carriers. Although the former view is favored,[3] the number of current carriers in both the (F) and (AF) states was obtained through Hall effect measurements to determine the actual mechanism of this resistivity change.

The observation of Hall effects in ferromagnetic materials has led to the establishment of the two Hall coefficients R_0 and R_1, the ordinary and extraordinary coefficients, respectively.[12] R_0 is related to the number of current carriers, and the interest in this investigation is centered on the value of R_0 for materials with (F) and (AF) magnetic ordering.

Measurements of the Hall voltage as a function of the magnetic induction were made at 297°K on Mn_2Sb and $Mn_{1.84}Cr_{0.16}Sb$. The former compound is ferrimagnetic and the latter antiferromagnetic at the temperature of measurement. A direct current method was used and the standard field-reversal technique employed. The Hall voltages were measured with a Keithley microvoltmeter, and the data analyzed by the method of Pugh and Rostoker.[12] For Mn_2Sb, $R_0 = 3.4\times10^{-12}$ V cm/AG and for $Mn_{1.84}Cr_{0.16}Sb$, $R_0 = 3.6\times10^{-12}$ V cm/AG. These positive Hall coefficients indicate a nearly filled band and represent an average carrier concentration of 1.0 hole per molecule. Since the charge carrier concentration at a given temperature is essentially the same for either the F or AF state, the difference in the resistivity of the two states must be due to the difference in the effective mobilities of the carriers.

Using the above data on the carrier concentration, and the room-temperature volume of the unit cell (two molecules) of 1.10×10^{-22} cm^3, the carriers per cm^3, N' are $1.8\times10^{+22}$. Since we expect this value to be independent of temperature, the value of the Fermi energy, $E_F(0)$, at absolute zero is defined by the equation[13]:

$$E_F(0) = (\hbar^2/2m)(3\pi^2N')^{2/3}.$$

Solving the above equation, we get $E_F(0) \cong 4\times10^{-12}$ ergs or about 2.5 eV.

SUMMARY

Investigation of the electrical properties of Cr-modified Mn_2Sb has been conducted to provide supplementary information to aid in understanding the unique magnetic properties of the system. The correlation between changes in resistivity and in magnetization which accompany the exchange inversion transitions shows that either will give essentially the same information on the transition temperature, the thermal hysteresis,

[12] E. M. Pugh and N. Rostoker, Rev. Mod. Phys. **25**, 151 (1953).

[13] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 249.

and $(\partial H/\partial T_s)_P$ values. Measurement of the shift in transition temperatures caused by external magnetic fields of different orientations to the tetragonal c axis has provided information on crystalline anisotropy of the intermediate magnetic state in agreement with the results from magnetization measurements.

Measurements of the Hall effect have shown that the number of current carriers is the same in both the ferrimagnetic and antiferromagnetic states, and this information has yielded a value of 2.5 eV for the Fermi energy at absolute zero.

ACKNOWLEDGMENTS

The author wishes to acknowledge helpful discussions with Dr. H. S. Jarrett and Dr. F. J. Darnell. The single crystal specimens were prepared by Dr. J. J. Cox and Dr. K. B. Keating of the Du Pont Engineering Research Laboratory.

PHYSICAL REVIEW VOLUME 132, NUMBER 2 15 OCTOBER 1963

Effect of Dipolar Fields on the Antiferromagnetic Spin-Wave Spectrum

R. LOUDON
Royal Radar Establishment, Great Malvern, England

AND

P. PINCUS*
Department of Physics, University of California, Los Angeles, California

(Received 7 June 1963)

The spin-wave dispersion relation for a simple uniaxial antiferromagnet is calculated, with inclusion of volume dipolar fields. The spin-wave spectrum is anisotropic and a degeneracy exists between the uniform antiferromagnetic-resonance modes and manifolds of short-wavelength spin waves, similar to the situation in a ferromagnet. The densities of states of these degenerate spin waves are calculated, and are then used to estimate antiferromagnetic-resonance linewidths caused by paramagnetic impurities having a different g value or exchange coupling to the host spins. Finally, the linewidth caused by surface pits in the sample is estimated.

I. INTRODUCTION

THIS paper is concerned with the effects of the classical dipole-dipole interaction between magnetic moments on the spin-wave spectrum of a simple uniaxial antiferromagnet. In ferromagnets, it has been known for some time[1] that the surface demagnetizing fields have a profound influence on the ferromagnetic-resonance frequency. Further, it has been shown by Herring and Kittel[2] that the volume dipolar fields cause the ferromagnetic spin-wave spectrum to become anisotropic. Anderson and Suhl[3] were the first to recognize that the surface demagnetizing fields give rise to a region of the spin-wave spectrum which is degenerate in frequency with the uniform ferromagnetic-resonance mode. The reason for this degeneracy is that, for spin waves with wavelengths short compared to sample dimensions ($kL \gg 1$), the signs of the magnetic poles on the surface giving rise to the transverse demagnetizing field oscillate rapidly in space. The transverse demagnetizing field is proportional to the number of uncompensated poles and is, therefore, small. On the other hand, the longitudinal demagnetizing field is large and leads to a reduction of the spin-wave frequencies so that some of the spin waves become degenerate with the uniform mode. This degeneracy allows crystalline imperfections[4] to mix the uniform mode ($k=0$) spin waves generated on resonance with the plane-wave ($k \neq 0$) spin waves in the degenerate manifold and thus gives rise to an important source of linewidth. Further, it has been shown by Suhl[5] that the premature saturation of the ferromagnetic-resonance[6] signal is due to coherent spin-wave scattering into the degenerate modes via the dipolar-anisotropy fields.

It is interesting to speculate about the importance of similar effects in antiferromagnets where there is no net magnetization and thus no bulk demagnetizing field. Keffer and Kittel[7] have indeed shown that the oscillating transverse moment generated in antiferromagnetic resonance (AFR) does give rise to a demagnetization shift in the antiferromagnetic-resonance frequency. This shift is, however, quite small compared to the ferromagnetic case. In ferromagnets $\delta\omega/\omega \approx NM_s/H$, which may be of the order of unity, where N is some appropriate demagnetization factor, M_s the macroscopic mag-

* This work was supported in part by the U. S. National Science Foundation.

[1] C. Kittel, Phys. Rev. **71**, 270 (1947); **73**, 155 (1948).
[2] C. Herring and C. Kittel, Phys. Rev. **81**, 869 (1951).
[3] P. W. Anderson and H. Suhl, Phys. Rev. **100**, 1788 (1955).
[4] A. M. Clogston, H. Suhl, L. R. Walker, and P. W. Anderson, J. Phys. Chem. Solids **1**, 129 (1957).
[5] H. Suhl, J. Phys. Chem. Solids **1**, 209 (1957).
[6] R. W. Damon, Rev. Mod. Phys. **25**, 239 (1953); N. Bloembergen and S. Wang, Phys. Rev. **93**, 72 (1954).
[7] F. Keffer and C. Kittel, Phys. Rev. **85**, 329 (1952).