1-1-1988

Ultrasonic attenuation due to Mn2+ spins in Zn1-xMnxSe and Cd1-xMnxTe at low temperatures

Robert A. Mayanovic

R. J. Sladek

U. Debska

Ultrasonic attenuation due to Mn^{2+} spins in $Zn_{1-x}Mn_xSe$ and $Cd_{1-x}Mn_xTe$ at low temperatures

R. A. Mayanovic,* R. J. Sladek, and U. Debska
Department of Physics, Purdue University, West Lafayette, Indiana 47907
(Received 4 February 1988)

We have measured the attenuation of ultrasonic waves with frequencies between 30 and 150 MHz in $Zn_{1-x}Mn_xSe$, with $x=0.37$ and 0.53, and $Cd_{1-x}Mn_xTe$ with $x=0.45$ and 0.60 down to 1.5 K. A wide, shear-wave attenuation peak occurred almost entirely below the spin-glass transition temperature. The peak was higher the larger the value of x or measuring frequency. It was comprised of three non-Debye components whose amplitudes and relaxation rate activation energies, E_i, were larger the higher the temperature of the component's summit. The E_i's were simple multiples of the Mn-Mn exchange integral. The highest-T component was increased by an applied magnetic field. We attribute most of the attenuation to relaxation of the ultrasonic strain-induced changes in the orientation of spins frozen into clusters. The spin-phonon coupling seems to be anisotropic since no attenuation peak was observed with longitudinal waves.

I. INTRODUCTION

Diluted magnetic semiconductors (DMS), also called semimagnetic semiconductors, formed by random occupation by Mn of some of the type-II cation sites in II-VI compounds have been subjected to extensive study[1] because of effects produced by the Mn ions. Among these is a transition from a paramagnetic to a spin glass (or at least frozen-in spin-disordered) state at a low temperature, T_{sg}, when the Mn content is large enough.

Since ultrasonic studies can provide information about ionic-spin behavior near magnetic phase transitions,[2] it was anticipated that such studies would be useful for elucidating the behavior of Mn spins in (II-VI)-based DMS.

Previous investigations in this laboratory discovered that a shallow, rounded shear-elastic-constant minimum occurred in $Cd_{1-x}Mn_xTe$ (Refs. 3 and 4) which extended from far above the spin-glass temperature, T_{sg}, down to the lowest temperature employed and had its lowest point near T_{sg}. This effect was analyzed[4] in terms of the first and second strain derivatives of the Mn-Mn exchange interaction and the magnetic contribution to the heat capacity.[5]

Since in wide-gap DMS the interaction between the Mn ions is due to superexchange via the nearest anion,[6,7] ultrasonic measurements were initiated by us on $Zn_{1-x}Mn_xSe$. Some of our early results on this system, including a shear-elastic-constant minimum like that in $Cd_{1-x}Mn_xTe$ and discovery of a shear-wave-attenuation maximum located mostly below T_{sg}, have been reported.[8,9]

In this paper we shall give a more complete account of ultrasonic attenuation in $Zn_{1-x}Mn_xSe$ at low temperatures and present new corresponding results for $Cd_{1-x}Mn_xTe$. In addition the influence of a magnetic field will be described. Our presentation will include an analysis of the shear-wave attenuation peak into three non-Debye components with relaxation times having activation energies which are simple multiples of the exchange integral in each DMS system.

II. EXPERIMENTAL DETAILS

Our $Zn_{1-x}Mn_xSe$ and $Cd_{1-x}Mn_xTe$ samples were obtained from boules grown by Debska. They were x-ray-oriented, cut, and lapped to have pairs of parallel faces which were perpendicular to simple crystallographic directions. The $Zn_{1-x}Mn_xSe$ samples, with $x=0.37$ and 0.53, had the hexagonal, wurtzite structure and were the same ones used in our recent investigation of their room-temperature elastic constants. Their characterization is given in a paper[10] devoted to that topic. The $Cd_{1-x}Mn_xTe$ samples with $x=0.45$ and 0.6 had the cubic, zinc-blende (sphalerite) structure. They were characterized by the methods used for our $Zn_{1-x}Mn_xSe$ samples, except that for $Cd_{0.4}Mn_{0.6}Te$ we used the concentration expected from the components used in growing it. Experience indicates that this nominal concentration is probably within $\pm 5\%$ of the actual one. Characteristics of the $Cd_{1-x}Mn_xTe$ samples are listed in Table I.

The attenuation of 2-μs wide pulses of ultrasonic waves with frequencies between 30 and 150 MHz was determined by superposition of a calibrated exponentially decaying wave form on the echo train using commercial (MATEC) electronic instrumentation. The ultrasound was generated by applying rf pulses to a quartz transducer bonded to the sample.

Temperature was achieved in a Pyrex or a (variable-temperature) metal double Dewar using liquid He and liquid nitrogen. Temperature was measured with commercial Ge and Pt resistance thermometers (to within about 0.010 K below 20 K and about 0.10 K above 20 K, respectively), except that for measurements when the sample was suspended in a 12-inch Varian magnet a commercial carbon-glass resistance thermometer was used both when the field was off and when it was on.

The elastic constant (or combination of elastic constants) involved in a given type of ultrasonic wave can be inferred by using information in the literature.[11]

In analyzing our ultrasonic data we did not correct for the dependence of sample dimensions on temperature

TABLE I. Characteristics of $Cd_{1-x}Mn_xTe$ samples and the ultrasonic modes employed.

x	Length (cm)	Density (g/cm^3)	Mode Propag.	Polariz.
0.45	0.3809	5.366	[110]	[110]
			[110]	[001]
0.45	0.5603	5.366	[100]	⊥[001]
0.6	0.3436		[110]	[001]

since results on II-VI compounds[12] indicated that such a correction would be negligible.

III. RESULTS AND DISCUSSION

Our attenuation measurements revealed that a broad, shear-wave-attenuation peak occurred in $Zn_{1-x}Mn_xSe$ with $x=0.37$ and 0.53 as a function of temperature. It was located almost entirely below T_{sg} with its highest point located at about $T_p \sim \frac{1}{2}T_{sg}$. The height of the peak and T_p increase with x and ultrasonic frequency. A figure summarizing these results is given in Ref. 8 and will not be reproduced here. However, the higher-frequency data contained in it, will be shown and subjected to analysis herein. This analysis was not made in Ref. 8.

Before discussing $Zn_{1-x}Mn_xSe$ results, we present Fig. 1 which summarizes our zero-magnetic-field results on $Cd_{1-x}Mn_xTe$. From Fig. 1 it can be seen that the attenuation of (fast) shear waves is similar to that summarized above for $Zn_{1-x}Mn_xSe$ (and shown in Ref. 8). (In neither $Cd_{1-x}Mn_xTe$ nor in $Zn_{1-x}Mn_xSe$ did longitudinal waves have an attenuation maximum like that observed with shear waves.)

Since the height of the shear-wave-attenuation peak and the temperature of its highest point (T_p) increased with x, we infer that it is due to the presence of Mn^{2+} ions and the fact that the spin-glass transition temperature increases with x.[5,13,14] From the increase of height and T_p with *frequency* we infer that a relaxation mechanism is involved. A relaxation effect is consistent with the fact that as temperature decreases, and the attenuation goes through its peak, the velocity of shear waves increases from its lowest point near T_{sg}.[3,4,8]

In order to analyze the attenuation peak we (1) deduced an excess attenuation $\Delta\alpha$ from our data by subtracting a background value equal to the approximately temperature-independent, experimental values which occur above about 35 or 40 K, and (2) plotted $\Delta\alpha$ as a function of the logarithm of the temperature for the highest measuring frequency we used for each sample. Figure 2 shows our results for $Zn_{0.47}Mn_{0.53}Se$. From Fig. 2, and a similar plot for $Cd_{0.4}Mn_{0.6}Te$, it can be seen that $\Delta\alpha$ contains features that a simple relaxation type peak would not have, and furthermore, that the highest part of $\Delta\alpha$ is increased by a magnetic field, H, whereas the piedmont regions at high and low temperatures are not raised by the field. In fact in $Zn_{0.47}Mn_{0.53}Se$, but not in $Cd_{0.4}Mn_{0.6}Te$, the low-T piedmont is even decreased by the magnetic field.

The location of the $\Delta\alpha$ peak below T_{sg} and the increase of its highest part by the field imply that a spin polarization effect is involved.[15] In zero field the polarization is that of a spin-spin product as described by a spin-glass order parameter[16] which increases with decreasing temperature below T_{sg}. The reduction in the low T piedmont by H may be due to the field suppressing a small spin fluctuation contribution to the attenuation.[15]

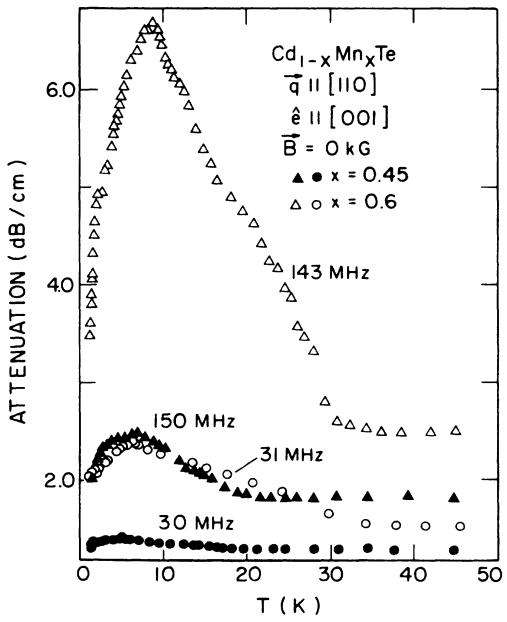

FIG. 1. Shear-wave attenuation vs temperature for $Cd_{1-x}Mn_xTe$ at frequencies between 30 and 150 MHz.

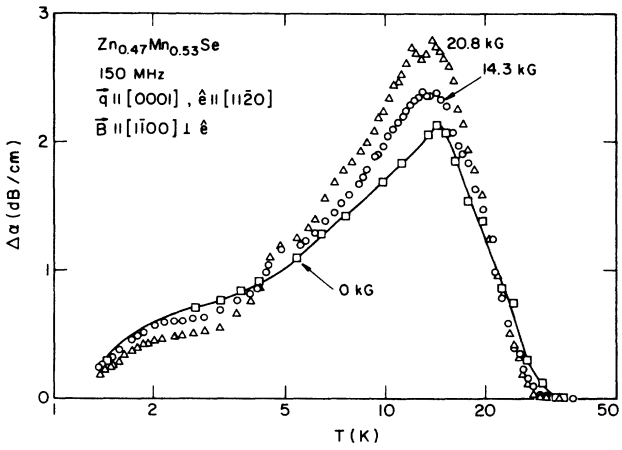

FIG. 2. Excess 150 MHz shear wave attenuation vs logarithm of the temperature for $Zn_{0.47}Mn_{0.53}Se$ without and with applied magnetic fields. A curve is drawn through the 0 kG data to aid the eye.

We have been able to fit our $\Delta\alpha$ data by means of an expression involving three non-Debye peaks each of which contains a universal relaxation function like that developed for dielectric relaxation[17] and used to fit ultrasonic attenuation in a superionic crystal.[18] The expression for $\Delta\alpha$ is

$$\Delta\alpha=\sum_{i=1}^{3}\frac{\omega A_i}{T}[(\omega\tau_i)^{-m_i}+(\omega\tau_i)^{1-n_i}]^{-1} \times\{f(T/T_{sg})+be^{-\gamma|T-T_{sg}|}\}\ , \quad (1)$$

where $f(T/T_{sg})=1-(T/T_{sg})^5$ when $T\leq T_{sg}$ and zero when $T\geq T_{sg}$, $\tau_i=\tau_i^0\exp[E_i/k_BT]$, with E_i the activation energy and k_BT Boltzmann constant times temperature. In Eq. (1), A_i, m_i, n_i, b, and γ are adjustable parameters with m_i and $1-n_i$ being between 0.35 and 0.60 for the various components of the various samples. The "universal" relaxation form[18] $[(\omega\tau_i)^{-m_i}+(\omega\tau_i)^{1-n_i}]^{-1}$ fitted the two lowest temperature components of $\Delta\alpha$ very well. However, the high T side of the highest ($i=3$) peak had a precipitous drop as T increased which is not describable by any reasonable relaxation form. This drop can be reproduced by the factor in the curly braces which we believe represents a sharp decrease in the correlation length for frozen spins as T_{sg} is approached from below. This factor represents a spin-glass order parameter which is not negligible until somewhat above T_{sg}. Its exponential tail represents the gradual breakup, with increasing T, of small spin clusters which persist above T_{sg}. There is evidence for such "frozen spin" clusters in the (mainly) paramagnetic phase above T_{sg} and of "loose" spins in the spin-glass phase of DMS which indicate that the spin glass transition is diffuse.[19,20] This diffuseness is, presumably, why the attenuation we observe differs from the sharp attenuation peak which occurs at the paramagnetic-antiferromagnetic transition in ordinary antiferromagnets due to the critical slowing in the relaxation of ultrasonically induced changes in the correlation between spin fluctuations.[15]

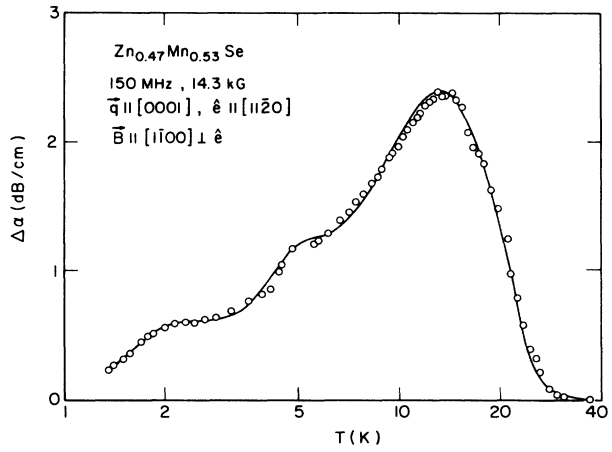

FIG. 3. Curve calculated from Eq. (1) to fit the 150 MHz shear wave excess attenuation (circles) in $Zn_{0.47}Mn_{0.53}Se$ in an applied magnetic field. These excess attenuation data were fitted because their quality was better than were those at zero magnetic field.

Figure 3 shows how Eq. (1) fits our $\Delta\alpha$ results on $Zn_{0.47}Mn_{0.53}Se$. Table II shows the values of the fitting parameters for this sample and for $Zn_{0.63}Mn_{0.37}Se$ and $Cd_{0.4}Mn_{0.6}Te$.

From Table II we can see that the m_i's and 1-n_i's are less than unity which would be the value characterizing a simple Debye relaxation process. This may indicate that

TABLE II. Parameters used in fitting Eq. (1) to attenuation vs temperature data. For $Zn_{0.47}Mn_{0.53}Se$ (ZMS1): $b=0.24$, $\gamma=0.26$ and $T_{sg}=24$ K. For $Zn_{0.63}Mn_{0.37}Se$ (ZMS2): $b=0.94$, $\gamma=0.26$ and $T_{sg}=15$ K. For $Cd_{0.4}Mn_{0.6}Te$ (CMT): $b=1.05$, $\gamma=0.18$ and $T_{sg}=24$ K.

Sample	Peak No.	m_i	$1-n_i$	E_i (meV)	τ_i^0 (10^{-12} s)	ωA_i $\left[\frac{dB\ K}{cm}\right]$
ZMS1	1	0.40	0.35	1.52	1.1	2.7
ZMS2	1	0.40	0.45	1.53	0.5	0.5
CMT	1	0.50	0.52	1.12	2.1	7.6
ZMS1	2	0.60	0.53	2.89	1.9	7.5
ZMS2	2	0.60	0.58	2.90	0.1	1.0
CMT	2	0.50	0.52	1.9	2.0	8.2
ZMS1	3	0.60	0.38	5.65	53.1	76.5
ZMS2	3	0.60	0.35	5.65	1.1	11.7
CMT	3	0.48	0.30	3.95	56.8	75.7

TABLE III. Ratios of $E_i/|J|$ and $\Delta E/|J|$. E_i is the relaxation-rate activation energy, $|J|$ is the absolute value of the exchange integral (1.12 meV for $Zn_{1-x}Mn_xSe$ and 0.69 meV for $Cd_{1-x}Mn_xTe$ taken from Ref. 6 and private communication with J. Spalek), and ΔE is the separation between the two lowest energy levels of two- and three-spin clusters (taken from Ref. 23).

Peak No.	$E_i/\|J\|$ $Zn_{1-x}Mn_xSe$ $x=0.37$ and 0.53	$E_i/\|J\|$ $Cd_{0.4}Mn_{0.6}Te$	Cluster type	$\frac{\Delta E}{\|J\|}$
1	1.35	1.6	pair	2
2	2.6	3.2	closed triangle	3
3	5.0	5.7	open triangle	5

collective processes[17] are involved or that each E_i and thus τ_i really has a range of values because of the random distribution of Mn ions in DMS. In that case our E_i's are average values. The values of $\tau_1^0(\sim 10^{-12}$ sec) are similar for all three samples and are also similar to the τ_1^0 values for $Zn_{0.37}Mn_{0.53}Se$ and $Cd_{0.40}Mn_{0.60}Te$. The values of A_i increase with i in all samples and are 5 to 7 times greater for $Zn_{1-x}Mn_xSe$ with $x=0.53$ than with $x=0.37$. This very large concentration dependence may indicate a cooperative effect since for independent spin pairs one would expect A_i to be roughly proportional to Mn ion concentration (provided that spin-phonon coupling is not strongly concentration dependent).

Although there is no suitable theory with which to compare our experimental results, we can interpret some of them in a semiquantitative fashion by utilizing theoretical results for ultrasound in spin glasses[21] and by considering effects due to the clustering of spins in DMS.

From Ref. 21 we expect A_i to be given by

$$A_i \approx 8.68 \frac{\sum_h R_h^2(\nabla_h J_h)^2}{\rho v^3 k_B} S(S+1) \tag{2}$$

where the h summation is over pairs containing ions with spin S located at $\mathbf{R}_i$ and $\mathbf{R}_j$, with $\mathbf{R}_h=\mathbf{R}_i-\mathbf{R}_j$, and an exchange integral $J_h=J_{ij}$; ρ is sample density, v is ultrasonic velocity, k_B Boltzmann's constant, and 8.68 converts to ($dB\ K\ cm^{-1}$) units. If we assume that the number of independent "active" spin pairs involved in peak 3 in $Zn_{1-x}Mn_xSe$ has the maximum possible value of $\frac{1}{2}$ the number of Mn ions and that $S=\frac{5}{2}$, we find that for an "average" pair $\mathbf{R}\cdot\nabla J=1.5$ meV$\approx 1.35|J|$ which is a reasonable value. The spin concentration assumed above is most likely an overestimate and thus the value of $\mathbf{R}\cdot\nabla J$ is an underestimate because of clustering. Evidence for the latter will be mentioned below.

A most interesting result of our $\Delta\alpha$ fits is that the relaxation rate activation energies, E_i, are simple multiples of the magnitude of the exchange integral (see Table III). These E_i values are comparable to the separation between energy levels in small-sized clusters[22] of Heisenberg spins as indicated in Table II. Alternatively, the E_i values may be related to the energy barriers against the inversion of Ising spins obeying Glauber dynamics.[23]

The energy level separations for Heisenberg spins are between the lowest and the next higher energy level in 2 spin and 3 spin clusters.[22] For a pair of spins this separation is $2|J|$, for a closed triad of spins it is $3|J|$, and for an open triad of spins it is $5|J|$. Application of a magnetic field can reduce the separation between one component of the multiple higher energy state which was degenerate in the absence of the magnetic field.

In the case of certain *clustered* Ising spins obeying Glauber dynamics,[23] the energy barriers are 0, $2|J|$, and $4|J|$, with these $|J|$ values defined to be twice as large as those in Ref. 22.

It should be noted that the above clustering effects were developed for, and applicable at, low Mn concentrations so that they may have only qualitative applicability to our samples. Another caveat is that Ref. 23 deals with Ising spins while Heisenberg spins (like in Ref. 22) would probably be more appropriate for our samples except that some anisotropy in spin-phonon coupling, if not in J itself, seems to be needed to account for our observing an attenuation peak with shear waves but not longitudinal waves.

Anisotropic superexchange might come about due to the effect of spin-orbit coupling (on the anion) via the Dzialoshinski-Moriya (DM) interaction[24] $\mathbf{D}\cdot[\mathbf{S}_1\times\mathbf{S}_2]$ where $D\sim\lambda J/U$ with λ the spin-orbit coupling, J the superexchange integral without spin-orbit coupling, and U is the energy between the occupied and empty Mn $3d$ energy levels. In fact EPR experiments have revealed anisotropic exchange attributed to the DM interaction.[25] It should be noted that to account for our results all that is needed is anisotropy in the derivative of the exchange energy rather than in the exchange energy itself.

In conclusion, we have presented low-temperature ultrasonic attenuation results on two dilute magnetic semiconductors which involve the relaxation of Mn^{2+} spin disturbances arising from strain-induced modulation by shear waves of the superexchange interaction between Mn spins.

ACKNOWLEDGMENTS

Thanks are due to the following colleagues at Purdue for stimulating discussions and for providing the magnet and its power supply: Professors J. K. Furdyna, R. L. Mieher, P. F. Muzikar, J. Spalek, and J. Kossut. The National Science Foundation Materials Research Laboratory Grant No. DMR84-18453 provided some financial support.

---

*Present address: Dept. of Physics, University of Notre Dame, Notre Dame, IN 46556.

[1]See, for example, J. K. Furdyna, J. Appl. Phys. **53**, 7637 (1982); and N. B. Brandt and V. V. Moschalkov, Adv. Phys. **33**, 193 (1984).

[2]B. Lüthi, T. Moran, and R. J. Pollina, J. Phys. Chem. Solids **31**, 1741 (1970).

[3]A. Y. Wu and R. J. Sladek, J. Phys. (Paris) **42**, C6-646 (1981).

[4]P. Maheswaranathan, R. Mayanovic, and U. Debska, J. Magn. Magn. Mater. **54-57**, 1225 (1986).

[5]R. R. Galazka, S. Nagata, and P. H. Keesom, Phys. Rev. B **22**, 3344 (1980).

[6]B. E. Larson, K. C. Hass, H. Ehrenreich, and A. E. Carlson, Solid State Commun. **56**, 347 (1985).

[7]J. Spalek, A. Lewicki, Z. Tarnawski, J. K. Furdyna, R. R. Galazka, and Z. Obuszko, Phys. Rev. B **33**, 3407 (1986); J. K. Furdyna, N. Samarth, R. B. Frankel, and J. Spalek, *ibid.* **37**, 3707 (1988).

[8]R. A. Mayanovic, R. J. Sladek, and U. Debska, *18th International Conference on Physics of Semiconductors, Stockholm, Sweden, 1986,* edited by O. Engström (World-Scientific, Singapore, 1987), Vol. 2, p. 1755.

[9]R. A. Mayanovic, R. J. Sladek, and U. Debska, Bull. Am. Phys. Soc. **32**, 810 (1987).

[10]R. A. Mayanovic, R. J. Sladek, and U. Debska, Phys. Rev. B (to be published).

[11]K. Brugger, J. Appl. Phys. **36**, 759 (1965).

[12]O. Caporaletti and G. M. Graham, Appl. Phys. Lett. **39**, 338 (1981) [HgTe, CdTe]; R. R. Reeber and G. W. Powell, J. Appl. Phys. **38**, 1531 (1967) [ZnS].

[13]A. Twardowski, C. J. M. Denissen, W. J. M. de Jonge, A. T. A. M de Waele, M. Demianuik, and R. Triboulet, Solid State Commun. **59**, 199 (1986).

[14]Y.-Q. Yang, Acta Phys. Sinica **33**, 1454 (1984).

[15]M. Tachiki and S. Maekawa, Prog. Theor. Phys. **51**, 1 (1974).

[16]S. F. Edwards and P. W. Anderson, J. Phys. F **5**, 965 (1975).

[17]A. K. Jonscher, Nature **267**, 673 (1977).

[18]D. P. Almond and A. R. West, Phys. Rev. Lett. **47**, 431 (1981).

[19]M. Escorne and A. Mauger, Phys. Rev. B **25**, 4674 (1982).

[20]G. Dolling, T. M. Holden, V. F. Sears, J. K. Furdyna, and W. Giriat, J. Appl. Phys. **53**, 7645 (1982).

[21]K. H. Fischer, Z. Phys. B **50**, 107 (1983).

[22]S. Nagata, R. R. Galazka, D. P. Mullin, H. Akbarezadeh, G. D. Khattak, J. K. Furdyna, and P. H. Keesom, Phys. Rev. B **22**, 3331 (1980).

[23]M. Cieplak, M. Z. Cieplak, and J. Lusakowski, Phys. Rev. B **36**, 620 (1987).

[24]T. Moriya, Phys. Rev. Lett. **4**, 228 (1960); Phys. Rev. **120**, 91 (1960).

[25]N. Samarth, Ph.D. thesis, Purdue University, 1986.